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## XXXIII. *On the Clark Cell as a Source of small Constant Currents.* By RICHARD THRELFALL, *M.A.*, *Professor of Physics, University of Sydney, and* ARTHUR POLLOCK, *B.Sc.**

[Plates VI. & VII.]

THERE are several methods by which the potential-difference (for the future written P.D.) of the plates of a voltaic cell may be measured. To measure the E.M.F. it is, as a rule, necessary to prevent the cell under examination from yielding any appreciable current while the estimation of its terminal P.D. is being made.

The electrometer is consequently the most obvious instrument to use in such an investigation; but, as a matter of fact, it is infinitely inferior both in convenience and accuracy to the galvanometer.

All the experiments about to be described were made with a galvanometer in the manner adopted by Lord Rayleigh and Mrs. Sedgwick (Phil. Trans. ii. 1884, "On the Electrochemical Equivalent of Silver, and on the Absolute Electromotive

* Read March 23, 1889.

Force of Clark Cells"). The method admits of an estimation of the terminal P.D. of a cell, either at rest or when (by the use of separate sets of resistance-coils to short-circuit its terminals) it is yielding a current of any desired value.

Let E be the E.M.F. of the cell, P.D. its terminal potential-difference, C the current passing through it, R its internal resistance, R′ the external resistance short-circuiting its terminal, Δ the observed change of P.D. at any instant when the current is flowing, measured from the value of P.D. when the cell is at rest. Then

$$\begin{aligned}\Delta &= \text{P.D. when cell is at rest} - \text{P.D. when cell is giving current C,}\\ &= E-(E-CR),\\ &= CR \text{ when there is no polarization.}\end{aligned}$$

Now at any instant let the E.M.F. change by polarization so that it becomes E′, and let the internal resistance become R″ Then, on short-circuiting,

$$\begin{aligned}\Delta &= E-(E'-C'R''),\\ &= E-\frac{E'R''}{R'+R''}.\end{aligned}$$

Consequently, if E′ diminishes or R″ increases, we shall have increased values of Δ. These increased values will then indicate what is generally known as polarization. It is possible, however, that there may be another sort of polarization (if we may venture to so extend the term) of which an increasing E′ or diminishing R″ is characteristic. If such an action exists and tends to increase as time goes on, we shall observe a continual decrease of Δ as time progresses after short-circuiting.

Such an effect has been pretty constantly observed ; and as it was not due to any change in the compensator, we are obliged to attribute it to a small variation in the Clark cell itself in one or both of the directions mentioned.

On referring to Wiedemann (*Die Lehre von der Electricität*, edition 1883, vol. ii. p. 708) we found a statement, on the authority of Hockin and Taylor (Journ. Soc. Teleg. Eng. viii. p. 282, to which we have not access), to the effect that an increase of thickness of a polarizing layer of hydrogen on mer-

cury causes the polarized surface to become more positive. The method employed, and the statement that finally bubbles of gas may be given off by sufficiently diminishing the area of the mercury surface, suggests that the polarizations used in the experiments were very strong. The electrolyte was dilute sulphuric acid.

Some experiments were made by us, using a similar but improved method and with zinc-sulphate solution as an electrolyte. The sort of effect we were in search of was an increase of potential on one mercury surface of about 0·0002 volt. Every precaution was taken in securing mercury and sulphate of zinc identical with those used in Clark cells, and in checking the behaviour of the electrodes. An effect larger than that we were in search of could generally be detected on altering the extent of the mercury surfaces, but we finally convinced ourselves that the capillary assumptions made were of such a nature as to require revision. This would in itself have involved extensive research, and we did not feel that the end was likely to prove in any way commensurate with the labour of reaching it; consequently we are unable to say whether the potential of the mercury surface does or does not rise with increased density of hydrogen deposition. In any case the small deviation of the value of $\Delta$ observed from its value, as accounted for by the cell resistance, shows that very little (if any) hydrogen really reaches the mercury surface. On the other hand, it is easy to see several reasons why $R''$ might become smaller sufficiently to account for the effect observed. It may be worth noting that the possibility of collecting evidence as to the existence or nonexistence of polarization when the change of $\Delta$ with flux of time is very small becomes a question of indirect evidence.

We did not habitually estimate changes of $\Delta$ of less magnitude than 0·000045 volt, and consequently what follows refers only to changes of greater amount than this. By our method the obvious test for polarization would be a measurement of the resistance of the cell at the actual moment when its terminal P.D. was obtained. This is experimentally impossible (as we consider) with the accuracy necessary, to say nothing of the continual changes in the value of the current taken from the cell which are to be expected during the

adjustment of the bridge. The tests which we apply can be rendered evident most easily by means of a diagram. Consider first the case of no polarization, *i. e.* no change of E or R. If we plot values of $\Delta$ as ordinates when C is nearly constant, and is assumed to be exactly so, and times reckoned from the epoch of short-circuiting as abscissæ, then the resulting curve will be three sides of a rectangle if it is prolonged till the moment of reinsulating the plates of the cell. This in fact corresponds simply to the case of $\Delta = CR$. Now let polarization set in. The curve giving the value of $\Delta$ will rise or fall, and the amount of rise or fall will be a sort of measure of the polarization.

Again, let currents of different values be taken from the cell and observe whether $\Delta = KC$, where K is a constant (it is of course assumed that R cannot be got with sufficient accuracy by other means, and the determining of it in this way would beg the question). We shall show that when certain conditions are complied with, this is nearly but not quite true. Consequently to the high degree of accuracy which has been aimed at in our experiments, it is never true to say that the Clark cell remains unpolarized when changes of K are considered as evidences of polarization. In order to exhibit the changes actually occurring in K, the following Table has been prepared. To get the value of C, corresponding to any observed value of $\Delta$, the experimental P.D. was taken and divided by the external resistance. The table shows what the cell variations actually are—expressed as if they were all to be traced to actual changes of resistance. It will be noticed that the values of K increase as the current diminishes, showing that what is ordinarily called polarization is less with greater currents than with small. It is fair, however, to state that the variations of P.D. in the latter case were nearer to our experimental limit of discrimination, and consequently are to be treated as having less weight than those referring to greater currents.

TABLE I.

Table giving the value of K from the equation $\Delta = KC$.

| Date. | External resistance. | Δ. | Terminal P.D. | Current. | K. | |
|---|---|---|---|---|---|---|
| 1888. | L. ohms. | volts. | volts. | amperes. | | |
| July 26 | 143 | 0·04730 | 1·38776 | 0·009704 | 4·874 | |
| 26 | 143 | 0·04590 | 1·38911 | 0·009714 | 4·725 | |
| 26 | 143 | 0·04545 | 1·38956 | 0·009717 | 4·677 | |
| 26 | 143 | 0·04606 | 1·38913 | 0·009713 | 4·741 | |
| 26 | 494 | 0·01593 | 1·41917 | 0·002872 | 5·545 | |
| 26 | 987 | 0·00729 | 1·42781 | 0·001446 | 5·039 | |
| | 1423 | 0·005217 | 1·430663 | 0·001005 | 5·189 | Mean of 13 obs. during July & Aug. |
| July 24 | 2862 | 0·00254 | 1·43323 | 0·0005007 | 5·072 | Mean of 2 obs. |
| 24 | 4293 | 0·00180 | 1·43383 | 0·0003339 | 5·384 | |
| Aug. 21 | 10000 | 0·00076 | 1·43538 | 0·0001435 | 5·295 | Mean of 2 obs. |
| Oct. 22 | 10000 | 0·00079 | 1·43448 | 0·0001434 | 5·507 | Mean of 4 obs. |
| July 31 | 20000 | 0·00058 | 1·43489 | 0·00007174 | 8·084 | |
| 31 | 30000 | 0·00045 | 1·43507 | 0·00004783 | 9·407 | |
| 31 | 40000 | 0·00036 | 1·43521 | 0·00003588 | 10·03 | |
| 31 | 50000 | 0·00027 | 1·43530 | 0·00002870 | 9·406 | |
| 31 | 60000 | 0·00023 | 1·43539 | 0·00002392 | 9·614 | |
| 31 | 70000 | 0·00023 | 1·43544 | 0·00002050 | 11·21 | |
| 31 | 90000 | 0·00018 | 1·43554 | 0·00001595 | 11·28 | |
| Nov. 1 | 10000 | 0·000630 | 1·42837 | 0·00014284 | 4·415 | Temp. 21°·6 C. Mean of 2 obs. |
| 2 | 10000 | 0·000765 | 1·42853 | 0·00014285 | 5·355 | Temp. 21°·7 C. |
| 1 | 10000 | 0·000630 | 1·42107 | 0·00014211 | 4·433 | Temp. 34°·2 C. |
| 1 | 10000 | 0·000630 | 1·42107 | 0·00014211 | 4·433 | Temp. 33°·9 C. |
| 1 | 10000 | 0·000630 | 1·42117 | 0·00014211 | 4·433 | Temp. 33°·0 C. |
| 1 | 10000 | 0·000720 | 1·42158 | 0·00014216 | 5·064 | Temp. 32°·0 C. |
| 1 | 1450 | 0·00293 | 1·41997 | 0·00097931 | 2·991 | Temp. 30°·9 C. |
| 1 | 1450 | 0·00257 | 1·41913 | 0·00097868 | 2·626 | Temp. 30°·6 C. |
| 2 | 1450 | 0·00315 | 1·42605 | 0·00098351 | 3·203 | Temp. 21°·7 C. |

It is, however, also true that polarization is never sufficient to cause an uncertainty of 0·5 per cent. in the value of a current of nominally ·001 ampere yielded by the kind of cell about to be described.

The greatest observed uncertainty during three months of continued testing and varying of conditions was 0·6 per cent.; of this probably only half at most was to be traced to polarization.

On an average the uncertainty did not exceed 0·1 per cent.; so that we consider that in stating that the Clark cell may be used with security to give currents of a value not differing by more than 1 per cent. from their nominal value we shall leave a really unnecessarily large margin for uncertainty in the actual value of a properly constructed external resistance.

In May 1888 we began to investigate the behaviour of the

Clark cell when giving small currents, with a view to applying it to the calibration at any time of a certain galvanometer which we had designed for one of the hospitals of Sydney. We were aware that the Clark cell had the reputation of being easily polarized, but this seemed to us probably to arise from the fact that the cells as usually made expose very small surfaces of zinc and mercury. We therefore constructed some cells of considerable size in order to find out whether our idea was or was not correct. The cells constructed and tested were the following:—

(1) A set of 40 test-tube cells of the ordinary pattern. The tube of each cell was three inches long and half an inch in internal diameter. The area of surface of mercury exposed was about 0·2 square inch or 1·3 square centimetre. The cells differed considerably from one another as regards resistance, the average resistance being about 40 l. ohms. The positive electrodes were bits of "pure" zinc rod as supplied by the dealers, $\frac{1}{4}$ inch in diameter, but of rather variable lengths. The areas of the zinc surfaces immersed differed considerably in the different cells. These cells were first set up in June 1886, and have been tested at intervals ever since. Their behaviour is quite satisfactory with the exception of that of No. 18, which was out by about ·001 volt from the beginning.

(2) Thirteen cells, similar to the above, made up in 1888 for the purpose of this investigation, and charged with a sample of the same mercury as used by Lord Rayleigh, *i. e.* taken originally from the same bottle. Our object in preparing these cells was to connect our work directly with Lord Rayleigh's measurements.

Two days after being set up, the mean E.M.F. of these 13 cells exceeded the mean E.M.F. of the 40 cells by 0·00045 volt.

Considering that the paste had not been neutralized, the agreement is closer than might have been expected.

(3) A cell, generally called the "master cell," made up in a glass cylinder about 12 inches high and $1\frac{3}{4}$ inch in diameter. The zinc plate, which was just small enough to pass down the cylinder, was cut from a sheet of ordinary commercial zinc, and had been amalgamated before being placed in the cell. The mercury surface was about three square inches in area. This cell was generally used to oppose the others.

(4) Two cells set up in glass jars similar to the above, but shorter and of greater diameter. Each of these cells exposed a mercury surface of about 12 square inches, and a zinc surface of nearly equal amount. As it was expected that considerable solution of zinc would occur in these cells, the plates were wrapped up in parchment paper. One of the cells was called the "large cell," and the other the "hospital cell," as it was actually in tentative use in the hospital during the progress of the testing, and was occasionally brought over by hand for comparison.

The investigation of the peculiarities of these cells was directed to the elucidation of the following points:—

1. The discovery of the most probable value of the E.M.F. of the cell at rest with a view to finding its terminal P.D. when yielding a given current.

2. The effect of the extent of mercury and of zinc surface in determining the maximum current which can be taken from any cell with a given allowable amount of uncertainty.

3. Does the value of $\Delta$ change with lapse of time reckoned from the epoch of short-circuiting? and if so what is the best time for making an observation?

4. Does the value of $\Delta$ change appreciably from day to day, the external resistance through which the cells are short-circuited remaining constant, or generally has the immediate previous history of the cell anything to do with the value of $\Delta$ in short-circuiting?

5. Has change of temperature any considerable effect on the value of $\Delta$, all the other conditions remaining constant?

6. The reliability of the large cell to give ·001 ampere through a platinoid resistance assumed correct at 15° C.

*Method of Experimenting.*—As already stated, the method described by Lord Rayleigh (*loc. cit.*) has been used throughout. All the measurements were made in a room with a southern aspect, and therefore not subject to any sudden change of temperature. Light was admitted through a sheet of paper forming a window in otherwise closed shutters. The temperature lay between 14° and 16° C. during the winter months, in which the experiments were made. At the close advantage was taken of a hot day to repeat the investigation at 23° C.

The galvanometer generally used had a resistance of about

six thousand ohms, and a sensitiveness of about four scale-divisions for $10^{-11}$ amperes by direct test. This was sometimes supplemented by another galvanometer of nearly sixteen thousand ohms resistance, and whose sensitiveness could be brought up to several scale-divisions for $10^{-13}$ amperes.

The smallest change of P.D. usually noted was that compensated by altering the resistance in the compensator by 0·1 ohm corresponding to 0·000045 volt.

In addition to the apparatus requisite for finding the terminal P.D. of any cell at rest, resistances were required for the purpose of short-circuiting the terminals of the cell. For this purpose a very large box of German-silver resistance-coils was used. All the coils had been previously compared with standards by Carey Foster's method, and were in fact adjusted by this method in the laboratory. The corrections are in no case large enough to require taking into account. The insulation of the various portions of the apparatus was carefully attended to by the use of blocks of paraffin and was very necessary.

For the determination of the most probable value of the E.M.F. of any cell, comparisons of all the cells were made by the method mentioned, and the mean value was taken as identical in absolute measure with Lord Rayleigh's mean value, *i. e.* 1·43500 Rayleigh volt at 15° C. Many complete comparisons were made during three months, partly to find the mean and partly to check the action of each cell. The large cell and hospital cell were compared with the small ones, sometimes directly and sometimes through the intermediary of the master cell. The changes of temperature occurring were too small to affect the difference between the cells within our limits of observation. One hundred and sixty comparisons were used in computing the probable values of the E.M.F. of the large cell and of the hospital cell at rest.

Nothing could have been more satisfactory than the behaviour of all the cells, though they were badly used between whiles. Suffice it to say that the result was almost the same whatever cell was used to oppose the others; and throughout the months of June, July, and August the mean E.M.F. of the large cell has the value of 1·43588 Rayleigh volt at 15° C., and the hospital cell the corresponding value of 1·434608 volt under the same conditions.

The second point referring to the effect of variable zinc and mercury surface on the observed values of $\Delta$ with varying currents was practically the first one to be investigated. Without going into the large amount of numerical information collected, we may state the following results:—

When the change of $\Delta$ during five minutes after short-circuiting is less than or equal to about $\frac{1}{10}$ per cent. of its value immediately after short-circuiting, the currents stand in about the order of the extent of mercury surface exposed. From a study of the small cells amongst themselves, it was found impossible to give any satisfactory explanation (of an experimental character) of the large difference of the maximum possible currents (*i. e.* those leading to a change of P.D. less than $\frac{1}{10}$ per cent.) that were observed.

The mercury surface was practically the same in all these cells, but the zinc surface varied. The currents did not stand at all in the order of the zinc surfaces. The most important factor appeared to be the thickness of the layer of mercurous sulphate, but it was not the only one. If the layer was less than about a quarter of an inch thick, the cells were bad. The result of it all was that the most important thing besides having plenty of mercurous sulphate is to have large surfaces of mercury and possibly of zinc. For this reason the large cells which it was intended to use in practice received the greatest share of attention, and we shall confine ourselves to describing the phenomena exhibited by them.

The results of some typical measurements are given in the following tables and curves, which will be found to contain information as to the effect of previous history as well. It may be stated that it was found possible to estimate the value of $\Delta$ within less than half a minute after short-circuiting.

From our point of view, viz. the applicability of the cell as a source of current of 0·001 ampere, it is immaterial whether there is polarization or not so long as it is not of a creeping character—nor then if the rate of creep is constant.

The answer to the third question is from the practical point of view absolutely vital and has received most attention.

Table II. gives the experience we have had. As a result the time finally chosen at which to make an observation is two minutes after short-circuiting. The information contained in the Table is also given graphically in Plate VI.,

where curves are drawn with values of Δ as ordinates and time as abscissæ.

In Plate VII. corresponding curves are drawn when the cell is yielding a current of nearly 0·01 ampere. They are drawn from observations taken on July 26 with a resistance short-circuiting the terminals of the large cell of 143 l. ohms. (See Table I.)

TABLE II.

Variations of terminal P.D. with time when large Clark cell is short-circuited through 1423 l. ohms.

Δ is the terminal P.D. immediately before changing the resistance between the poles from ∞ to 1423 l.o. minus the terminal P.D. at the times given in the 2nd column.

| Date. | Time. | Δ. | Resistance between Poles. |
|---|---|---|---|
| 1888. | h m s | volts. | |
| July 24. | 3 30 0 | 0·000000 | Changed from ∞ to 1423 l. |
| | 30 20 | +0·004095 | 1423 [ohms. |
| (1.) | 32 0 | +0·004815 | 1423 |
| | | steady at this. | |
| | 35 0 | ..... | Changed to ∞. |
| | 37 0 | +0·000595 | ∞ |
| | 40 0 | +0·000405 | ∞ |
| | 45 0 | +0·000360 | ∞ |
| | 51 0 | +0·000360 | ∞ |
| July 24. | 3 57 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 57 20 | +0·004635 | 1423 |
| (2.) | 59 0 | +0·004500 | 1423 |
| | 4 2 0 | +0·004500 | 1423 |
| | 4 0 | +0·004500 | 1423 |
| | 5 0 | +0·004500 | 1423 |
| | 6 0 | +0·004500 | 1423 |
| | 7 0 | ..... | Changed to ∞. |
| | 7 20 | +0·000135 | ∞ |
| | 9 0 | 0·000000 | ∞ |
| | 10 0 | −0·000045 | ∞ |
| | 12 0 | −0·000090 | ∞ |
| | 15 0 | −0·000135 | ∞ |
| | 23 0 | −0·000135 | ∞ |
| July 26. | 3 7 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 7 20 | +0·005805 | 1423 |
| (3.) | 8 55 | +0·006030 | 1423 |
| | 10 0 | +0·006120 | 1423 |
| | 11 45 | +0·006120 | 1423 |
| | 12 0 | ..... | Changed to ∞. |
| | 13 10 | +0·000405 | ∞ |
| | 14 20 | +0·000315 | ∞ |
| | 16 0 | +0·000315 | ∞ |

Table II. (*continued*).

| Date. | Time. | Δ. | Resistance between Poles. |
|---|---|---|---|
| 1888. | h m s | volts. | |
| Aug. 8. | 3 17 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 18 0 | +0·006588 | 1423 |
| (4.) | 20 20 | +0·006499 | 1423 |
| | 22 20 | +0·006454 | 1423 |
| | 25 45 | +0·006409 | 1423 |
| | 26 0 | ..... | Changed to ∞. |
| | 27 0 | +0·000269 | ∞ |
| Aug. 8. | 3 30 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 31 0 | +0·006230 | 1423 |
| (5.) | 34 45 | +0·006185 | 1423 |
| | 35 0 | ..... ... | Changed to ∞. |
| | 35 20 | +0·000226 | ∞ |
| Aug. 9. | 12 57 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 57 40 | +0·006819 | 1423 |
| (6.) | 58 40 | +0·006685 | 1423 |
| | 1 1 0 | +0·006640 | 1423 |
| | 2 0 | ..... | Changed to ∞. |
| | 3 0 | +0·000315 | ∞ |
| Aug. 20. | 5 17 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 17 30 | +0·005227 | 1423 |
| (7.) | 18 30 | +0·005182 | 1423 |
| | 20 20 | +0·005114 | 1423 |
| | 22 2 | +0·005047 | 1423 |
| | 22 10 | ..... .. | Changed to ∞. |
| | 23 0 | +0·000180 | ∞ |
| | 25 0 | +0·000090 | ∞ |
| Aug. 20. | 5 25 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 25 30 | +0·005024 | 1423 |
| (8.) | 26 0 | +0·004979 | 1423 |
| | 34 45 | +0·004822 | 1423 |
| | 35 0 | ..... | Changed to ∞. |
| | 35 30 | +0·000090 | ∞ |
| Aug. 21. | 4 5 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 6 0 | +0·004906 | 1423 |
| (9.) | 7 20 | +0·004821 | 1423 |
| | 10 0 | +0·004726 | 1423 |
| | 10 0 | ..... | Changed to ∞. |
| | 10 30 | +0·000180 | ∞ |

Table II. (*continued*).

| Date. | Time. | Δ. | Resistance between Poles. |
|---|---|---|---|
| 1888. | h m s | volts. | |
| Aug. 21. | 4 12 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 12 45 | +0·004636 | 1423 |
| (10.) | 13 20 | +0·004591 | 1425 |
| | 15 0 | +0·004551 | 1423 |
| | 15 0 | ..... | Changed to ∞. |
| | 16 0 | +0·000045 | ∞ |
| Aug. 21. | 4 19 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 19 15 | +0·004641 | 1423 |
| (11.) | 21 0 | +0·004551 | 1423 |
| | 21 0 | ..... | Changed to ∞. |
| | 22 0 | +0·000090 | ∞ |
| Aug. 21. | 4 25 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 25 40 | +0·004546 | 1423 |
| (12.) | 26 10 | +0·004505 | 1423 |
| | 28 0 | +0·004505 | 1423 |
| | 28 0 | ... ..... | Changed to ∞. |
| | 28 20 | +0·000135 | ∞ |
| Aug. 21. | 4 30 0 | 0·000000 | Changed from ∞ to 1423 l. o. |
| | 31 0 | +0·004551 | 1423 |
| (13.) | 36 0 | +0·004551 | 1423 |
| | 36 0 | ..... | Changed to ∞. |
| | 37 0 | +0·000135 | ∞ |

The scale of the curves is very big in order to bring out differences of observed values of Δ; it will be noticed, however, that Δ was in all cases extremely small.

The general effect is seen to be a decrease of Δ as time goes on from the epoch of short-circuiting. This has already been discussed. For comparison a large Daniell cell was examined at the same time, and the dotted curve in Plate VII. referring to it will show its unexpected inferiority. The cell exposed about 80 square inches of copper, and was allowed to work long enough to obtain a clean electrolytic surface; zinc-sulphate solution was used in the inner cell. The resistance of the cell was very low, and the curve taken is for its behaviour when short-circuited through 143 l. o. This gives a current of about 0·0067 ampere; and a current-density of 0·000012 ampere per square centimetre of copper. In the

large Clark cell the curve for a current of about 0·01 ampere (condemning the cell for so great a current) corresponds to a current-density of 0·00012 per square centimetre of mercury surface. The more nearly corresponding curves, taking current-density as the criterion of correspondence, are to be found by using one of the Clark-cell curves for 0·001 ampere. In this case the latter is infinitely superior, and is even superior when giving 0·01 ampere with ten times the current-density. The trouble and difficulty involved in setting up a Daniell cell would quite independently render it useless for our purpose, so the comparison was on all accounts pushed no further.

It will be noticed that the greatest fall of terminal P.D. was observed on August 9th and amounted to 0·006685 volt, being 0·001468 greater than the mean. Now, on July 26th occurred the smallest observed value of the cell at rest, this was 1·435415 volt. Suppose that in practice these causes of error (here observed on different days) conspired, we should have taken a real P.D. of 1·428730 volt for 1·430663 volt. The error thus introduced would have been ·002 volt nearly, or an error of about 0·14 per cent.

Similarly taking the greatest observed terminal P.D. at rest and the smallest fall, the error the other way if these causes conspire amounts to calling a real P.D. of 1·43186 only 1·430663, or about 0·08 per cent.

It remains to discuss the effect to be expected from changes of temperature. The temperature-coefficient of the Clark cell is of course known, but we have as yet given no evidence as to any possible temperature-change of $\Delta$ other than what is to be expected from the known change in the cell itself. To test this matter, on November 1st the large cell was placed in a very large vessel filled with water at a temperature of about 38° C., and left there for a considerable time. The bath was well wrapped up, and during 37 minutes the temperature fell to 34°·2 C. when tested by a standard thermometer. The fall of temperature being so slow allows us to hope that the temperature of the cell during the experiments did not differ to any considerable extent from that of the water. Moreover the E.M.F. of the cell had again become constant and had fallen through 0·00729 volt. By comparison with the 40 cells, on October 20th, it was found that the E.M.F. of the

master cell was 1·43356 volt at 17° C. By a comparison of the large cell with the master cell at the time of the experiment and at a temperature of 21°·5 C., its E.M.F. was found to be 1·42900 volt; consequently at 34°·2 C. the E.M.F. was 1·42171 volt. The results are given in Table III.

TABLE III.

Fall of terminal P.D. of Large Cell when short-circuited through 10,000 l. ohms.

| Date. | Temperature. | Δ. |
|---|---|---|
| 1888. November 1 | 21·6 C. | volt. 0·000675 |
| „ 1 | 21·6 C. | 0·000585 |
| „ 2 | 21·7 C. | 0·000765 |
| „ 1 | 34·2 C. | 0·000630 |
| „ 1 | 33·9 C. | 0·000630 |
| „ 1 | 33·0 C. | 0·000630 |
| „ 1 | 32·0 C. | 0·000720 |

Fall of terminal P.D. of Large Cell when short-circuited through 1423 l. ohms.

| Date. | Temperature. | Δ. |
|---|---|---|
| 1888. November 1 | 30·9 C. | volt. 0·002925 |
| „ 1 | 30·6 C. | 0·002565 |
| „ 2 | 21·7 C. | 0·003150 |

The result to be noted is that the value of Δ may be said to have changed in the practical case from 0·005 to 0·003 volt between 15° and 30° C.—a very small variation considering the complexity of the changes which might have taken place; consequently we need not fear that any ordinary change of temperature will introduce any appreciable error except that arising from the ordinary temperature-coefficient of the cell.

This experiment gives incidentally the value of the temperature-coefficient for rapid heating over the range comprised between 21°·7 and 30°·9 C. Assuming Lord Rayleigh's temperature-coefficient for the range of temperature between 15° and 21°·7 C., *i. e.* for temperatures which had been acquired so slowly as to allow the zinc-sulphate solution to reach its proper concentration with complete certainty, we have the following :—

Lord Rayleigh's formula is

$$E = 1{\cdot}435\,[1 - 0{\cdot}00077\,(t - 15°)\,],$$

whence it follows that (calling the mean E.M.F. of the 40 cells at 15° C. = 1·43500 volt) at 17° C., the temperature of comparison, the mean E.M.F of the 40 cells is 1·43279 volt ; and hence the E.M.F. of the master cell, as it was 0·00077 volt greater than the mean of the 40 cells, = 1·43356 volt. At 21°·5 C. the E.M.F. of the master cell (using Lord Rayleigh's coefficient) = 1·42859 volt.

At the time of the experiments on the large cell the temperature of the laboratory was 21°·5 C. and E.M.F. large cell − E.M.F master cell = + 0·000405 volt ; therefore E.M.F. of large cell = 1·428995 volt at a temperature of 21°·5 C. Thirty-seven minutes after having been put in the bath the E.M.F. of the large cell was steady at 34°·2 C. and E.M.F. large cell − E.M.F. master cell = − 0·006885 volt, the master cell being still at 21°·5 C. Hence the fall of E.M.F. of the large cell for a rise of 12°·7 C. was 0·00729 volt, and its actual E.M.F. was 1·4217 volt.

Hence taking our standard temperature at 21°·5 C., and using Lord Rayleigh's formula with the constant appropriate to 21°·5 C., we have

$$1{\cdot}4217 = 1{\cdot}42900\,\{1 - K \times 12{\cdot}7\},$$

whence K = 0·000402 between 21° and 34° C. say, and for rapid heating.

There is no reason why this value, deduced from a somewhat rapid change of temperature, should agree with the value obtained by Lord Rayleigh in cases where the temperature varied much more slowly and was considerably lower. We have evidence from the history of the 40 cells to the effect that at all events up to 24° C. the *differences* of E.M.F.

are practically the same as they are at 15° C. In the case to which these results have been applied the external resistance through which the cell has to work is composed partly of a copper and partly of a platinoid resistance-coil. The copper coil in this case belongs to the galvanometer and the error thereby introduced, though well within the limits laid down for this particular application, is much greater than it would have been had the galvanometer-winding consisted of German-silver or platinoid wire. There would in this or similar cases have been no objection to the use of such a winding.

At 15° C., then, to get the most accurate current of 0·001 ampere from the large cell we ought to use an external resistance of 1430·7 l. ohms, if we ignore the difference between the Rayleigh volt and the Congress volt, as we may very well do.

It is now left for us to determine what error a change of temperature of 8° on either side of 15° C. is likely to cause. In this country, New South Wales, we have to work pretty often at temperatures as high as 23° C., and we imagine that no one would work below 7° C. if it could be avoided; consequently we take these as our limits.

We have already found that perturbations of the P.D. of the cell itself may introduce an error in that quantity to the extent say of 0·2 per cent. (the greatest we got by combining the most aberrant observations of different days was 0·14 per cent.).

On the strength of the experiment above 30° C. and the experience with the small cells from 14° to 23° C., we assume that no change in $\Delta$ will occur otherwise than that dependent on the ordinary coefficient. This is not strictly legitimate for lower temperatures, but it is difficult to obtain them much lower here.

We know that we shall have two causes at work tending to change our current value; these will be in the same direction.

The E.M.F. will tend to diminish with increased temperature, and the resistance of the wire will increase.

The cell-resistance change is of course included in variations of $\Delta$, and these we have shown to be negligible for practical purposes when the external resistance is large.

By combining the effects of change of resistance and of

E.M.F. (using Lord Rayleigh's coefficient) we get a temperature-coefficient for the current yielded.

The temperature change of resistance of platinoid wire is about 0·022 per cent. per degree, and the change of E.M.F. when the cell rises or falls 8 degrees from 15° C. is about 0·0088 volt. Consequently the error arising from this cause is about 0·6 per cent. Adding all the possible causes of error together we find that the uncertainty *may* arise to 0·96 per cent., say 1 per cent., in the value of the current. It need hardly be added that of these causes of error the two latter are easily allowed for where accuracy is required, and the former is very small. We do not think that in such a case an error of more than 0·1 per cent. ought to be expected.

For ordinary purposes for which the current may be used an accuracy to within 1 per cent. is probably all that will be required.

We have to thank Lord Rayleigh and Prof. Ayrton for some valuable suggestions as to the mode of statement of the above results.

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## XXXIV. *On the Application of the Clark Cell to the Construction of a Standard Galvanometer.* *By* Professor Richard Threlfall, *M.A.**

[Plate VIII. figs. 1 & 2.]

In the instrument which forms the subject of this paper the experience obtained with Clark's cell is utilized to obtain a simple means of standardizing a working current-measurer. The construction of the instrument itself will be readily understood from the accompanying figures. Its chief features are :—

(1) The arrangements which have been made for the support of the controlling magnet and for its adjustment : this latter can be readily carried out without disturbing the suspension.

(2) The damping of the needle by means of a thin copper cylinder attached to a bit of fine wire and dipping in clove-oil.

(3) The mechanical arrangements of this part of the appa-

* Read March 23, 1889.

ratus, allowing of the easy suspending of the mirror and adjustment of the cylinder in the oil.

(4) The arrangements for the testing of the galvanometer by means of the Clark cell.

(5) The curving of the scale, so as to obtain direct tangent-readings from a scale of equal parts.

The single coil of the instrument consisted of a rectangular section of winding of 200 turns of No. 22 B.W.G. copper wire. Resistance 2·02 ohms at 16° C.

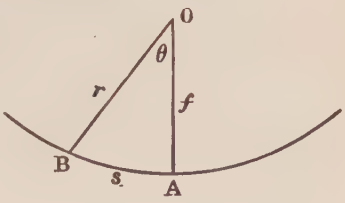
This coil had an axial dimension of 1·3 centim., a radial dimension of 1·3 centim., and the radius of the inner layer of winding was 3·7 centim. The coil was supported so as to be capable of sliding backwards and forwards with respect to the suspended parts, keeping parallel with itself to a considerable degree of accuracy. The slide was of carefully crossed wood, the moving portion being kept in its position in the grooves by means of half carriage-springs at each end. A somewhat similar arrangement is adopted in the sliding wooden parts of the Kew magnetometer.

There are three marked positions of the coil with respect to the suspended needles.

Though the mirror is rather large the magnets are small, in the ordinary sense, *i. e.* about a quarter of an inch long. A calculation was made by Mr. Adair on the law of deflexion of the magnet by the coil at the three distances and up to deflexions of about 15°. The method adopted in this calculation was the expansion in 'Spherical Harmonics' used by Maxwell, part 4, chap. xiv. The tangent law was found to be practically true, *i. e.* the deviation from it would never introduce an error of more than about ·5 per cent. The error was greater the less the deflexion, and was negligible for the accuracy required, which was of course not very great. The error arising from partly neglecting the torsion of the silk fibre was also investigated and found to be without influence: the fibre was seven inches long.

The divided scale was one of Elliott's scales, in which 360 divisions correspond to 229 millimetres. The distance from the mirror to the scale was 1095·7 scale-divisions, or about seven hundred millimetres. The problem of finding the form of the curve into which it is necessary to bend the scale of

equal parts so as to read direct currents was solved by Mr. Adair ; as we could find no previous record of this solution, I will give it here.




Let A B be a portion of the curve required ; let O A $=f$ the apsidal distance, $\theta$ the polar angle subtended by A B, O B $=r$ the distance of the light-spot from the mirror. The incident light falls along A O. A B $=s$.

The form of the curve, assuming that the galvanometer obeys the tangent law, is

$$s=2f\tan\frac{\theta}{2},$$

or

$$\frac{ds}{d\theta}=f\sec^2\frac{\theta}{2};$$

and the differential equation giving $r$ in terms of $\theta$ is

$$\left(\frac{dr}{d\theta}\right)^2+r^2=f^2\sec^4\frac{\theta}{2}.$$

This is insoluble in general terms : but if the range of $\theta$ is small we can develop in powers of $\theta$, and assume $r=f+\lambda$, where $\lambda$ is the addition to the radius of the circle whose centre is O and radius $f$. Thus the differential equation for $\lambda$ becomes, by retaining terms in $\theta^4$,

$$\frac{1}{f^2}\left(\frac{d\lambda}{d\theta}\right)^2=\left[2\left(\frac{\theta}{2}\right)^2+\frac{7}{3}\left(\frac{\theta}{2}\right)^4\right]-2\frac{\lambda}{f}.$$

Writing $\lambda'$ for $\frac{\lambda}{f}$, we get

$$\frac{d\lambda'}{d\theta}+\left[\frac{\sqrt{2}}{\theta}-\frac{7\sqrt{2}}{48}\theta\right]\lambda'=\frac{1}{\sqrt{2}}\left[\theta+\frac{7}{48}\theta^3\right];$$

hence

$$\lambda'=\theta^{-\sqrt{2}}e^{\frac{7\sqrt{2}}{96}\theta^2}\left[c+\int\theta^{\sqrt{2}}\left\{1-\frac{7\sqrt{2}}{96}\theta^2\right\}\frac{1}{\sqrt{2}}\left\{\theta+\frac{7}{48}\theta^3\right\}d\theta\right]$$

Now $\lambda'=0$ when $\theta=0$; therefore the arbitrary constant $c=0$;

and to the order of $\theta$ retained we get

$$\lambda' = \frac{\sqrt{2}-1}{2}\theta^2 + \frac{4-\sqrt{2}}{96}\theta^4$$
$$= \cdot 207\,\theta^2 + \cdot 0269\,\theta^4.$$

At the extremity of the scale $\theta$ is about $\frac{1}{3}$ in circular measure; thus at the end of the scale,

$$\lambda' = \cdot 0233,$$

and $\lambda = 25 \cdot 5$ scale-divisions.

Thus on the radius making the angle $\theta = 19^\circ\ 6'$, whose circular measure is $\frac{1}{3}$, the theoretical curve is outside the circle by a distance of 16 millim. Similarly, when $\theta = 10^\circ = \cdot 174$ radius, $\lambda' = \cdot 006297$, and therefore $\lambda = 6 \cdot 901$ scale-divisions $= 4 \cdot 4$ millim.

With these numerical results the curve was laid out on millimetre paper, a template was cut to the curve, and the wooden back of the scale-holder was brought up to the template. The scale itself was carefully pinned to the wood at short intervals along its whole length.

The Clark cell supplied with the instrument had the same area of surface as the "large cell" referred to in our previous papers: it was tested from day to day alongside of the large cell, master cell, &c. The following particulars refer to this testing.

Internal resistance (August 28, 1888), roughly 5·5 ohms. August 29, at 16° C., hospital cell − master cell $= -0 \cdot 000852$ volt. Terminal E.M.F. hospital cell, two minutes after short-circuiting through 1426 legal ohms, taking E.M.F. of master cell at 1·435:—

| | | |
|---|---|---|
| August 28. | 1·4263 | volt. |
| „ 29. | 1·4261 | „ |
| „ 29. | 1·4262 | „ |

About ten minutes after short-circuiting, in each case the E.M.F. fell further ·0011 volt.

As the galvanometer was very dead-beat no calibration-experiment need take longer than 20 seconds, so that this is without effect.

In order to use the instrument the cell is coupled up in series with a platinoid resistance of 1417 legal ohms; the

galvanometer-coil being itself 2·02 ohms, the cell about 5·5 ohms. Consequently the current used in testing is

$$c = \frac{1{\cdot}4262}{1417 + 2{\cdot}02} = {\cdot}001007 \text{ ampere.}$$

This is quite near enough for our purpose.

In order to set up the galvanometer once for all the following dispositions were made. The galvanometer-coil was pushed up towards the suspended magnet as far as it would go; this was known as position O. The controlling magnets were then raised so as to give a mean sensitiveness; the known current was put on and reversed and the double deflexion noted. This deflexion was indicated by a fiducial mark on the scale. If at any time the sensitiveness of the instrument changes, it is only necessary to bring the coil up to its O position and raise or lower the controlling magnets by means of the adjusting arrangement till the deflexion reaches the fiducial mark.

When the coil is in the position A, ·001 ampere corresponds to 10 scale-divisions; and at B, to 1 scale-division. These points were found by using a very large storage cell, whose E.M.F. was tested whilst the calibration was going on, and employing suitable resistances from a thick wire box. The whole arrangement was tested by this means from ·001 to ·4 ampere, and it was found that the results were wonderfully consistent: this was possibly in part due to the mirror not being very good, and consequently the observation is so far wanting in accuracy. With the rather bad light-spot the readings could not be taken nearer than to about 1 per cent. at the end of the range, and 3 per cent. towards the centre. Of course if currents of only three or four milli-amperes are to be measured, these can be got with at least this accuracy by using the coil at some convenient point near O, A and B being rather far away. As an accuracy to about 5 per cent. is all that is requisite in measuring currents for hospital work, there can be no doubt that this instrument fulfils the purpose for which it was made, having an accuracy in use of at least five times this amount. I have to thank the assistants in my laboratory for the excellency of their workmanship.

## XXXV. *The Measurement of High Specific Resistances.* By R. Threlfall, *M.A., Professor of Physics, University of Sydney, N.S.W.**

[Plate VIII. fig. 3.]

The experiments which form the subject of this paper were begun almost immediately after my arrival in New South Wales, in June 1886, and have been continued at intervals ever since. The original object was to measure accurately the resistance of certain gums produced by trees growing in the Colony. The only gum thoroughly examined however, up to now, is that produced by the "grass tree" (*Xanthorrhœa hastilis*). This gum, in spite of many attempts to improve it by various methods of purification and by mixing with other substances, turns out to be useless as an insulator, having in fact no higher resistance than, say, ordinary samples of resin, that is about $4{\cdot}1 \times 10^3$ megohms per cubic centimetre. Besides this, the gum in question is faulty in other ways. It is of the nature of shellac, but cannot compete with the shellac as ordinarily supplied either in price or purity. In addition it has the two fatal defects of being partly soluble in water and of decomposing before it melts. Long-continued gentle heating does not seem to improve it in this latter respect; while the texture of the material becomes looser, it grows friable and very dark in colour. Benzoic acid appears to be given off in large quantities during the process. In spite of many attempts I have hitherto failed to obtain any considerable quantity of the fig-tree gums which are said to be produced in large quantity in the northern parts of the Colony. This paper therefore will be devoted to a description of the method adopted in measuring these resistances, a method which ultimately reached a considerable degree of perfection; partly on account of the modifications introduced in the construction of high-resistance galvanometers, and partly on account of the peculiar property of Clark cells. The method has since been employed for other measurements, as will be shown later on.

* Read March 23, 1889.

I do not wish to claim any superiority for the galvanometer over the electrometer methods, except that, given the galvanometer and cells, it is certainly more easily applied, especially when the determinations are numerous. I was forced to adopt the galvanometer method in this instance through not having an electrometer; but I was by no means unwilling to do so, because I have long been of the opinion that the galvanometer as usually constructed is susceptible of considerable improvement for delicate work by simply pushing the ordinary conditions of sensitiveness nearer to their limit.

## General Description of Method.

### *Measurement of Resistance of Gums.*

The substance to be tested forms a layer of very exactly estimable dimensions between two plates of conducting material. The experiment consists in obtaining equal deflexions of a sensitive galvanometer—(1) when a known fraction of the E.M.F. of a Clark cell is allowed to act through a megohm in the galvanometer circuit; and (2) when the E.M.F. of a known number of compared Clark cells is allowed to act through the resistance to be measured.

The apparatus, therefore, consists of the plates with the substance to be investigated, the galvanometer, the standard cells, and a megohm.

### *The Resistance-plate Arrangement.*

This consists of two brass plates accurately rectangular and scraped flat on one surface. The dimensions of the plates I used were—length 15·2 centimetres, breadth 12·7 centim., thickness 1·6 centim. These rather exact numbers were obtained by filing. The measurements were made ($\alpha$) by beam compasses, ($\beta$) by the dividing-engine. Neither the corrections which had to be introduced for temperature nor the comparison of the dividing-engine scale and the beam compasses with the standard metre are given, as no absolute measurements of pure substances have been made. Several measurements of each plate were made by both methods. The surfaces were made flat by scraping, and this process was continued till the contact was sufficiently perfect for one plate to lift the other when laid on it, both surfaces being clean in the

ordinary sense. The upper plate is furnished with a solid handle something like the handle of a flat-iron, and is pierced by three holes, through which pass the micrometer-distance screws (see Plate VIII.). The screws are 4 centim. long, and the threaded portion is ·55 centim. in diameter (they would have been better if twice the diameter). The micrometer-heads are divided into a hundred parts each, and the mean pitch of the screw, as determined by a comparison with the millimetres of a standard scale by means of a measuring microscope, is 39·5 divisions to a millimetre; that is, one turn is equal to ·5063 millimetre at 20° C. The points of the screws are conical, and the distance from the end of the thread to the point of the screw is 5 centim. The screws are of steel tempered to the blue, the heads of brass; and the tap used to produce a thread in the holes through the brass plate was identical with one of the screws; the lathe being set to use the same part of its screw and of its change wheels during the making of each. The measurement showed that the screws were very good especially in the middle portion; they were also practically exactly alike. The goodness of the fit in the brass plate was shown by the fact that an increase of temperature of 20° C. was sufficient to "bind" the screws very perceptibly. Indices similar to the indices of spherometers were erected in the upper plate of the apparatus—one index for each screw. All the workmanship being accomplished, the plates were next platinated by a process given in Gore's 'Electro-metallurgy' under the name of "Roseleur's Process;" a previous experiment showed that when the directions are faithfully carried out, this process will yield a hard bright deposit of platinum. The bath, however, is very troublesome to keep in order since no solution of platinum takes place to supply the place of that deposited. To prepare the plates for platinating, they were first heated to the temperature of boiling water and rubbed on the scraped surfaces with a solution of caustic potash. Finally, they were rubbed with a bit of fine pumice dipped in dilute caustic potash. This is by far the best laboratory method known to me for preparing surfaces of brass for electro-plating; a clean surface is obtained with comparatively little abrasion. Before I found this out, I was much troubled to secure a good deposit.

After platinating, care being of course taken to prevent the deposit being unequal, the plates were carefully washed and dried. It was noticed that the metallic surfaces were covered with a faint bloom of black platinum. On placing the plates together and moving the top one slightly, the lower plate at once adhered, and though weighing several pounds could easily be lifted by the upper one. On pulling the plates apart the "bloom" was found to be burnished practically all over both surfaces, showing of course that the platinating had not sensibly altered the planeness of the surfaces. For this accuracy I am much indebted to the university assistant, Mr. James Cook, who, being accustomed to prepare optically flat surfaces, was led by the application of experience gained in that way to the happy result above mentioned.

The exact position of the two plates with respect to one another was secured by cementing the plated surfaces together with hard paraffin. Two lugs of thick brass were made fast by screws to each plate, and brought as near to one another as consistent with leaving an air insulating space between them. These were then bored to fit slightly conical steady pins. A rim was also screwed round the lower plate, so that when the top plate was removed the bottom plate resembled a tray. The rim projected about ·8 of a centimetre on each side of the surface, and extended to a height of about half a centimetre above it.

The gum was introduced between the plates in the following way. The micrometer-screws were carefully cleaned and screwed through their holes till they made contact with the lower plate; the point of contact was almost as easy to estimate as in the ordinary use of the spherometer. At all events three or four consecutive attempts to fix the point of contact did not differ from each other by more than about one half of one of the micrometer-divisions. The accuracy with which the contact-point can be fixed depends mainly on the workmanship of the screw, which must fit perfectly "tight and free," to use the mechanic's very expressive term. The contact-points having been found, they were permanently scratched on the micrometer-heads and called zero points. The next operation consisted in screwing each of the screws through a known number of turns. In one experiment this

amounted to making the distance of the plates apart = ·02 centim.; and in another the distance was reduced to ·01 centim. with equally good results. It is not advisable in any absolute measure to reduce the distance to much less than this, because the error of the micrometer, depending as it does (as in this case) chiefly on the small irregularities of the screw, must not be allowed to become sensible. There is no doubt, however, that with first-rate appliances the micrometers might be easily made a hundredfold as accurate as mine, and their travel actually measured *in situ* by a suitable reading-microscope. In this case it would be important to make the screw portion much thicker to avoid any risk of permanent distortion (twisting) when the screws are finally screwed back while partly held by the gum*.

The screws being adjusted, the plates are slowly heated in a gas-oven till some gum laid on the surface of the lower one is in a state of quiet fusion. The great object is to avoid any distortion of the plates. With this aim in view the plates described were cast about twice as thick as they finally required to be in order that the "shell," supposed to be in a different state of strain to the interior, might be approximately removed. The plates were planed first on one side and then on the other till the right quantity of metal was removed; the last cuts being taken very fine. The handle affixed to the upper plate was of course arranged so as to fit loosely, and not in any way constrain the free expansion and contraction of the plates; the temperature having been often violently changed (by heating for cement &c.), it is hoped that the plates may be considered fairly well annealed. There is no doubt, however, that for complete satisfaction in an absolute measurement the plates should be capable of being optically examined during the process of heating. This would require to be done in the gas-oven or other uniform field of temperature and at the time the experiments were made. I had not the requisite appliances.

It was found by several trials that the best way of obtaining a layer of gum free from bubbles between the plates, was to

* Since this was written an improvement of the above micrometer-screw has been devised, entirely getting rid of the difficulty here referred to.– Oct. 3, 1889.

float the lower plate or tray pretty full of gum, and also to obtain a layer of gum free from bubbles and in quiet fusion on the upper plate. In the case of the grass-tree gum this could only be obtained by heating the gum for some time at a temperature higher than the one at which it was when the plates were brought together. This was accomplished much in the same way as is sometimes done in microscopy—when the cover-slip is placed on the slide with one edge down and the other end gradually lowered. The freedom from bubbles of the layer of gum obtained in this way was tested by allowing the plates to cool, and then heating the lower one till its surface reached the temperature of the melting-point of the gum, the upper one being kept cool. This being done the upper plate could finally be lifted, leaving only a small portion of the gum on the lower plate—owing to the small heat-conductivity of the gum. The layer of gum was left thick on one occasion for the purpose of this test, and when the manipulation described above was properly carried out there were no bubbles; the layer in fact was very homogeneous indeed. The only danger left so far as the insulating material is concerned is that it may tend to crack away from the plates during cooling. In the cases examined this did not seem to be the case, because in the first place a thick layer of the same substance rapidly cooled on a thin plate showed no tendency to crack. Again, a great many insulating substances are more or less plastic, or rather viscous, down to temperatures very nearly approaching those at which experiments are usually made (in this country 23° C. is a not unusual temperature). Again, the massiveness of the plates being considerable no distortion of them ought to be caused by the gum, if the ordinary precaution of allowing them to cool slowly be observed.

In the experiments hitherto made the cooling took place during the night in the gas-oven, which being coated with non-conducting material took a long time to cool. On the other hand, in all experiments of the sort one is in a dilemma. If the substance is placed between conducting-plates there are dangers of the kind mentioned; if, on the other hand, the material itself be worked with a view to making it take a prescribed form, the difficulties, especially in the measurement

of its thickness, become great. I began by making some attempts of this kind, using blacklead to make the gum-surface conducting, and plating this electrolytically. The difficulties arising in the shaping of the plates are, however, practically prohibitive with friable material. Besides this I have often noticed that in electrotyping it is difficult to prevent the deposit being "spotty" at first, and this has shaken my faith in the perfect continuity of ordinary blacklead surfaces. Possibly platinating with an induction-coil may be really the best way.

However, to finish the description of the case in point:—The gum was carefully scraped away from the edges of the plates as soon as they were cool, and the screws were screwed back. This could not be done with any ease at first because of the cementing action of the gum. This was got over by heating the head of the screw with a Bunsen flame: finally, the screws were retracted far enough to be quite out of the way*. A correction to the area of surface has of course to be made for the three screw-holes. If the thickness of the gum be considerable compared with the diameter of the hole, this may be very complicated. In the present case it was negligible. Thus the whole area of the gum-plate was 193·04 centim. less the area of the three screw-holes —·7128 centim., *i. e.* 192·3272.

Now it is clear that, owing to the curvature of the lines of flow round the edges of the holes, the real correction will be less than the one made. The deposit of gum, however, is pierced by a hole corresponding to the conical end of the screw and, consequently, only very small.

Finally, the steady pins are taken out of the plates and the gum is ready to be measured.

In order to measure the resistance of good insulation by means of this arrangement, it is clear that it will be advantageous to have a galvanometer of the highest degree of sensitiveness. This is desirable both because the thicker the

* Note, Dec. 1888.—The difficulty is, however, serious, and has led to new hollow screws being made. Through the holes bored down the centres of the screws gold-plated copper rods pass; these are pinned to the screws till it is required to retract them; the ends of the screws themselves are flush with the lower surface of the upper plate, or very near so.

insulating layer the less will be the experimental error in the determination of its thickness; and the smaller the electromotive force required the less will be the difficulty of estimating it exactly, as will be shown in the proper place. I therefore attempted to obtain sensitiveness by pushing the ordinary conditions further than is usually done. My first experiments were on a galvanometer of about 9000 ohms' resistance, made by the Cambridge Scientific Instrument Company. It was soon very evident that when the current reached the value of about $10^{-7}$ ampere, the torsion of the suspension became important. My first modification was to increase the length of the fibre to about 12 inches; this led to considerable difficulty of adjustment, but increased the sensitiveness about fiftyfold. It then became clear that the next step must be to get the magnets more perfectly astatic and to reduce the weight of the mirror. The reducing of the weight of the mirror turned out to be more difficult than I anticipated; however, it was finally arrived at, and at the same time the astaticism was made more perfect. Some experiments showed that it was very difficult to get two sets of steel bars of the kind ordinarily employed even reasonably astatic. The difficulty lies partly in the magnetizing and partly in obtaining exactly equal quantities of steel in the two systems of magnets. In fact it is necessary that the steel bars be magnetized *in situ*, otherwise they can hardly be perfectly arranged and are sure to demagnetize each other more or less. Now when the two magnet systems are only separated by a bit of aluminium, say three inches long, it is impossible to thoroughly magnetize one system without demagnetizing the other more or less. Consequently it is necessary to set up an arrangement so that both systems can be magnetized at once. The following is a description of the arrangement adopted:—It consists of two small electromagnets with extremely soft cores, and movable pole-pieces most carefully worked so as to fit the ends of the cores. Every precaution was taken to make the electromagnets as much alike as possible; the iron was cut off the same rod, it was bent to the same templet, the annealing of both cores was done in a box of asbestos at the same time. The four brass bobbins carrying the wire were also made as much alike as possible,

and the same number of turns of wire were put on each bobbin by means of a revolution-counter. The winding was quite uniform, No. 18 B.W.G. wire being used. As a check the resistances of the bobbins were measured, when it fortunately happened that two were about one half per cent. higher than the other two, and so they were paired. The wire, it need hardly be added, was wound on to the four coils under a constant strain. The two electromagnets were then mounted on a permanent stand—one being kept steadily in a fixed position, and the other being capable of sliding parallel to a line drawn perpendicular to the lines joining the centres of the poles of each magnet. The pole-pieces were bevelled off from the top side; but the area of the ends remained large compared with the size of the magnets to be magnetized. The condition as to equality of quantity and quality of steel in the galvanometer magnets was next considered. After some reflection I decided that the most probable way of securing equality would be to discard bar-magnets entirely and use disk-magnets. I therefore procured a small piece of sheet steel about as thick as ordinary thin writing-paper, and had a die constructed so as to stamp small disks from this sheet. The sheet was fairly hard, and it was found that the disks "stamped" better when the sheet was taken in its natural state than when it was softened. A considerable number of disks were stamped out of the sheet, and these were then laid on a bit of flat iron and raised together to a bright red heat; they were then plunged together into a jar of cold water. On examination they all seemed to be glass-hard, and some of them remained flat. The four flattest ones were chosen and prepared for mounting. A bit of aluminium wire was cut to the right length and beaten out flat at each end. The disks were then cemented with shellac varnish, one on each side of each flattened end of the aluminium wire. The wire was thus much more accurately the centre of rotation of the magnetic system than is generally the case. Attempts were then made to get a good light mirror. About three ounces of small microscope cover-slips were examined by aid of the reflected image of the bars of a window, and from these about twenty were selected and silvered by the Rochelle salt process. They looked very

good, but on mounting for trial without strain they all turned out disappointing. I finally made use of a small portion of a larger mirror that had got broken. This was cemented on to the flat surface of one of the steel disks and was found not to be sensibly distorted. After trying very many cements, I incline to think that nothing is better than a trace of slow-drying white paint. Amongst other experiments I tried cementing two very thin glass disks together, selected so as to mutually correct each other by the drying of the cement. I also tried a method of using plaster of Paris. As plaster of Paris expands on setting I covered the back of a thin mirror with a layer of it about $\frac{1}{12}$ in. in thickness on drying, this of course forced the mirror into a concave form. The back of the plaster was rubbed away on a fine file till it was only about $\frac{1}{20}$ in. thick, and the mirror still remained very concave. Since cementing magnets on to disks with shellac varnish invariably forces the mirror to become convex, I hoped that I should obtain a correction of the concavity produced by the plaster by the convexity which the shellac tends to provoke. My anticipation was completely realized ; the mirror on examination turned out all that could be desired, but, alas, was too heavy for the purpose for which I required it. I can, however, most strongly recommend the process to anybody who desires a mirror to be flat and does not mind it being heavy. The best way is to use very little plaster and then to leave the mirror concave. This concavity can be removed by painting on small successive films of shellac ; it must be remembered that shellac films go on contracting for several days after they cease to be sticky. Equally good results can of course be obtained by cutting out (with a rotating tube and emery) disks of the size required from previously examined thin sheet glass. The surfaces generally require regrinding. The advantage of the process described is that it enables thin cover-slip glass, which is generally to hand, to be kept flat.

The mirror having been mounted on the steel disks, these last were magnetized by the apparatus mentioned above. In carrying out this operation the following precautions have to be observed:—

1. The distance between the pole-pieces requires to be the

same for each magnet. This was attained by setting them to touch a carefully prepared brass rectangular bar.

2. To annul the effect of any small outstanding differences between the cores of the magnets the current was supplied to them in multiple arc, and was strong enough to magnetize the cores beyond the saturation point.

The approximate moment of inertia of the magnet system was easily calculated, and it was found that the astaticism was at least ten times as good as the best I had been able to obtain with small bar-magnets mounted on mirrors or mica, and magnetized with a small horseshoe magnet. Of course, as has been pointed out by several observers, there is danger of rapid variation of the magnetization ; but it was thought better to risk this than to force it by artificial "ageing" by heating or otherwise. As will be seen hereafter, the magnets were never exposed even during the experiments to anything but the smallest electromagnetic forces, and the controlling magnet was weakened and introduced from high above the galvanometer, and only lowered sufficiently just to make its influence on the combination really felt. This is a delicate operation with ordinary arrangements, but becomes simple when the construction of the galvanometer is modified in a way to be explained directly. If one desires to keep the astaticism perfect, it is necessary to be mindful not to use the controlling magnet so as to produce demagnetization ; nor must the currents through the galvanometer ever rise to much greater values than those corresponding to the effects to be observed. From an examination of the investigation in Maxwell, vol. ii. articles 437 and 438, both Mr. Adair and I came to the conclusion that the disk form of magnet would retain its magnetization pretty well. This has turned out to be the case, for after more than a year's hard use, for all sorts of purposes, the galvanometer has still a sensitiveness of about one division for $10^{-9}$ ampere. The galvanometer is in daily use for testing cells with a view to their application to the resistance measurements at present under discussion.

This galvanometer, however, never came to be relied on to measure currents of less than $10^{-8}$ to $10^{-9}$ ampere. In the course of reading on the subject I consulted the paper by Messrs. T. and A. Gray in the Proc. Roy. Soc. 1884, vol. xxxvi.

p. 287. These gentlemen made use of a new arrangement of magnets and coils, which, however, can hardly be understood without referring to the picture, *loc. cit.* The coils and magnets were so arranged that the poles of the magnets were normally situated in conical holes containing the axes of the coils. The two horseshoe magnets were suspended from a frame of aluminium wire by one or two silk fibres of considerable length. The coils themselves were composed of very fine wire and had a high resistance. I lost three months' hard work in making and testing this arrangement, which certainly has the advantage of being practically perfectly astatic. The suspended arrangement being rather large was most troublesome to mount and balance, and had the additional disadvantage of having so great a moment of inertia that its period of vibration often amounted to 70 or 80 seconds. This sluggishness had the property of making it most difficult to use, for it was hardly possible to distinguish the motion due to the electromagnetic forces from the never-ceasing motion due to air-currents. Though the instrument was well-protected by a glass case, and this generally supplemented by a wooden box, I never succeeded in eliminating the effect of air-currents, though it must be added I never succeeded well enough with it in other respects to make it worth while to apply the "subjective" method of mirror observation. In any case it seems to be essential to have a means of adjusting the coils to the magnets as well as the magnets to the coils; but the adjustments are very tiresome even with the facilities which in the later forms of this instrument I had for making them. My coils had not quite so much wire as those of the Messrs. Gray because I used all I had and could get no more in Australia. However, the aggregate number of turns amounted to 59,900, and the resistance at 20° C. was 15,852 B.A. units, as against 62,939 turns and a resistance of 30,220 ohms attained by the authors quoted. The authors also state that the wire was approximately uniformly distributed throughout their coils, though in my case this was found impossible, keeping the external dimensions quite constant, and therefore there was a slight difference between the coils, which, however, was compensated for by their arrangement in the instrument. I do not think that the diminution of the

number of turns had much effect, because the diameter of the coils had reached 5·8 centim. Feeling that my non-success was probably to be traced to my inferior skill as an experimentalist, I undertook a long series of trials with a view to discovering the best way of hardening the magnets and their best position in the coils when at rest; amongst other experiments the following will do for description. Three bits of Stubb's steel wire were carefully cut and filed to a uniform length of $4\frac{1}{16}$ in., their diameters being $\frac{3}{64}$ in. These will be called A, B, and C. A was made glass-hard throughout; B was hardened through a distance of from $\frac{3}{4}$ to 1 inch at each end; C was hardened from a distance of from $\frac{1}{8}$ to $\frac{1}{4}$ inch at each end. These bits of wire were then magnetized by being placed between the massive poles of a very large electromagnet. The cores of this magnet were 3 inches in diameter and about 25 inches long. The pole-pieces were very broad and thick. The magnetization of the steel was carried nearly to saturation, and the magnets were found by filings to be free from consequent poles. On taking the times of vibration the following numbers were obtained :—

| | | | | |
|---|---|---|---|---|
| A | made 25 vibrations in | | 125 | seconds. |
| B | „ | „ | 124 | „ |
| C | „ | „ | 105 | „ |

After remagnetizing the magnets with about half as much current again round the electromagnet, it was found that

| | | | | |
|---|---|---|---|---|
| A | made 25 vibrations in | | 123 | seconds. |
| B | „ | „ | 107 | „ |
| C | „ | „ | 107 | „ |

B therefore was improved; A and C remaining about the same. The deviations were probably produced by the unavoidable shaking and jarring in mounting the magnets, though this was done with considerable care.

These magnets were next observed with respect to their behaviour with one of the coils. Coil "No. 3" was selected for this purpose. It was placed on the table, and above it hung a specially fine spring-coil of wire forming part of a Jolly's balance. The magnets were hung from the end of this spring by a loop of silk, and could be adjusted to penetrate the coil to a greater or less extent. In general five positions were taken :—

Position 1. Magnet-end flush with the upper windings of the coil.

„ 2. Magnet-end at $\frac{1}{4}$ of the length of the hole through the coil.

„ 3. Magnet-end at the centre of the coil.

„ 4. Magnet-end at $\frac{3}{4}$ of the length of the hole through the coil.

„ 5. Magnet-end flush with the bottom of the coil.

Three Leclanché cells were allowed to run for four hours through the coil before the experiment began. The coil had a resistance of 3130 ohms.

First, a series of observations was taken by observing on the glass scale the equilibrium position of the magnet with the current direct and reversed. The magnet was then lowered to position 2, and so on; then it was reversed and the experiments repeated. Two complete sets each way were made for each magnet, *i. e.* forty observations of distance and forty reversals of current. The experiment was a very pretty one, and I never remember to have seen any apparatus work better. The following set is given as a sample from the note-book. The numbers, of course, have no significance except with respect to the actual coil and magnet taken.

Magnet B.

| Position in Coil. | Double displacement with current + and −. | Number of experiments. |
|---|---|---|
| At edge of coil . . . | ·43 centim. | 3 |
| $\frac{1}{4}$ way in . . . . . | ·77 „ | 2 |
| $\frac{1}{2}$ „ . . . . . | 1·03 „ | 2 |
| $\frac{3}{4}$ „ . . . . . | 1·159 „ | 2 |
| Near bottom of coil . . ($\frac{1}{8}$ inch off) | 1·04 „ | 2 |

Magnet B reversed, otherwise everything the same.

| Position. | Displacement current + and −. | Number of experiments. |
|---|---|---|
| At edge . . . . . | ·415 centim. | 2 |
| $\frac{1}{4}$ way in . . . . . | ·78 „ | 2 |
| $\frac{1}{2}$ „ . . . . . | 1·085 „ | 2 |
| $\frac{3}{4}$ „ . . . . . | 1·27 „ | 2 |
| $\frac{1}{8}$ off bottom . . . . . | 1·11 „ | 2 |

The net result was that all the magnets behaved best when they started from three quarters to the whole way in, and that B was best, C almost as good as B, and A distinctly the worst. On reducing the observations it turned out that the ratio of the mean displacements of A and B was about ·782, while the ratio of the magnetic moments was ·755. This relation is of about the order one would expect, seeing that the length of the magnets was about 9·6 centim. and the dimensions of the coil were :—axial 3·8 centim., radial at one end 2·4, radial at other end 2·5. The external surfaces of the coils were cylindrical.

The ratio of the greatest displacements was ·643. It may be conceded, therefore, that the questions of magnetization and placing received a fairly complete answer. In the final arrangement of the galvanometer with horseshoe magnets, like those described by the Messrs. Gray, the length of the yokes of the magnets was 8·5 centim., and thus this was the distance between the centres of the coils. The legs of the magnets were 3·8 centim. long, and they were magnetized like the trial magnet B. When in position, the magnet-legs projected into the coils to an extent of about $\frac{7}{8}$ the axial dimension of the latter. The suspension was two washed silk fibres (one would not carry the load) 16 centim. long.

The test for sensitiveness was made by running a large Clark cell (already described) through 10,000 legal ohms, and a certain small resistance taken out of an ordinary Bridge-box. The terminals of the Bridge-box were coupled up through the galvanometer to a megohm. The accuracy of this method of testing has been already established.

The distance from the galvanometer-mirror to the scale was 155 centimetres ; and the light-spot was very good, showing the wire image as sharply as the lines on the scale. The scale itself was divided into millimetres. In the final test the period of vibration of the magnet system was 80 seconds, and the resistance out of the Bridge-box was 100 ohms. The E.M.F. acting through the megohm and galvanometer and 100 ohms was therefore $\frac{100}{10100}$ Clark cells, say ·0145 volt. The current was therefore $\frac{\cdot 0145}{116000} = 1{\cdot}26 \times 10^{-7}$ amperes.

Employing the method of vibrations and neglecting the correction for the extremely small log. decrement, the battery being of course reversed and several experiments made, it was found that the double deflexion amounted to 5 scale-divisions (millims.). Hence the deflexion corresponding to $1{\cdot}26 \times 10^{-7}$ amperes is 2·5 divisions. Now I do not think that, bearing in mind the lengthy period of the system, it would be possible to read to more than ·5 division. The difficulty comes in in eliminating air-currents ; as far as the scale went I could read certainly ·2 division, so there is no advantage to be gained in having the scale further, or even so far away. We may therefore say that five times the least measurable deflexion is given by $1{\cdot}26 \times 10^{-7}$ amperes, or that the least measurable deflexion itself is given by $2{\cdot}5 \times 10^{-8}$ amperes. This, I may mention, is only to be obtained when the magnets are judiciously kept from swinging by an extra controlling magnet, worked carefully from a distance till the vibrations get small, so as to jam against the side of the coil. Some fine quartz threads were also prepared by Boys' method, but no appreciable improvement introduced by their use could be detected. This may, however, have been on account of their thickness ; for they could be seen, with a little practice, in a good light, and when laid on a bit of black silk. I therefore came to the conclusion that neither I nor my instrument-maker (who is fairly good) could hope to compete in such delicate work with the Messrs. Gray, who, using this type of galvanometer, attained a sensitiveness of one half millimetre-division with a current of about $10^{-11}$ amperes, and that with a scale fairly close to the instrument, and with a manageable period of vibration.

In consequence of this failure I determined to use the four coils constructed for the Gray galvanometer, for an experiment in which they were employed in the usual manner. They were therefore roughly mounted, and provided with an astatic combination of the kind previously described. The results were so encouraging that the same methods were pursued further. In the final form the suspension was a quartz fibre, 85 centim. long, suspended in a carefully chosen glass tube. With such long suspensions the tube must be very straight, and the arrangement for raising and lowering the

suspended parts must be very good. After trying several arrangements for this, I adopted a pointed piston working into the tube and passing through a stuffing-box. The coils were of course anything but suited, as far as shape goes, for their present arrangement; however, they did what was requisite, though I have no doubt that coils might be made to increase the sensitiveness tenfold.

The mirror was in this case suspended midway between the magnets, and, for want of a better, was so thin that it got a little pulled out of shape by the paint which was used to fasten it to the aluminium wire. This fortunately turned out to be an advantage in some respects, for the vertical wire and the paint on the back of the mirror, by a happy accident, made the figure of the mirror practically that of a portion of a cylinder with a vertical axis; consequently, using a very good lens of 40 inches' focus, a good image of the light-spot was obtained at a distance of three metres. It became evident at once that the two real difficulties in securing sensitiveness lay in preventing air-currents and in adjusting the controlling magnet.

The first was finally attained by making the instrument practically air-tight; and, by means of a diaphragm, stopping down the beam of light to very nearly the size of the mirror —in this case of about 1 centimetre diameter. During the measurement of the resistance of an impure sample of sulphur this protection against air-currents was found to be insufficient, and the galvanometer was further protected by enclosing it in a cardboard box. If it ever becomes necessary to make an instrument to be sensitive to, say, $10^{-13}$ amperes, I shall have the support for the controlling magnet absolutely independent of the galvanometer-case, so that any vibrations set up in adjusting the magnet shall be transmitted only through heavy masonry. In the galvanometer now being described the controlling magnet could be raised by a nut and screw combination, itself sliding on a brass tube attached to the case of the instrument. The glass tube containing the fibre was clamped at its upper end to a very heavy stand of brass and lead, and this practically sufficed when the sensitiveness got to be of the order of one division to $10^{-11}$ amperes.

The arrangement for adjusting the distance of the control-

ling magnet was arrived at after several trials It consisted of an apparatus sliding and clamping on the brass tube, with a nut and screw for fine adjustment. It was intended to use a worm-wheel and screw for the adjustment in a horizontal plane; but this was found after a little practice to be unnecessary, although it would be convenient.

The details of this arrangement for raising and lowering the magnets will be understood from the drawing of the galvanometer for medical purposes on Pl. VIII. figs. 1 and 2, see p. 247, *suprà*. Many experiments were made in order to decide the relative merits of quartz and silk fibres. At first it was thought that silk did as well; but after a time a great deal of trouble with the zero was traced to the silk, and attempts were made to use finer quartz threads. In this, owing to the skill acquired by Mr. Pollock, I was finally successful. As I have had about a year's experience in drawing quartz threads, I add the following notes on the process in hope that they may prove of use to others. The difficulty is to get a large enough bit of quartz fused onto a suitable handle. The best way of managing this is first to heat a bit of rock crystal red-hot in an ordinary crucible and keep it heated for about an hour. On cooling, it will be found to have split into fragments of all sizes; one of these is chosen, and supported on a bit of lime or on a massive bit of iron, and is then fused under the oxyhydrogen (not oxy-coal gas) jet. When it has once been got glass-like it never cracks again, no matter how suddenly it may be heated. Porcellanous quartz draws into rotten threads, as might be expected. Two bits of fused quartz having been prepared they may be fused to the ends of two bits of clay tobacco-pipe, and can then be manipulated in the oxyhydrogen flame without trouble. There is no difficulty (when once the short thick threads have been drawn by hand) in the subsequent shooting. I most cordially indorse all that Mr. Boys says in favour of this admirable invention.

Another difficulty lies in the obtaining of a reasonable degree of astaticism. It has already been shown that it is practically possible to increase the astaticism of a magnetic combination by careful methods of magnetization and manufacture of the magnets: but the astaticism thus in general obtained is by no means perfect. The investigation of this

matter was undertaken by Mr. Adair, and proved to be difficult and unsatisfactory. In the first place it was necessary to determine the coefficient of torsion of the silk fibre to be used in the experiments. This fibre was about thirty inches long, and before mounting had been boiled in a tube of water. A copper disk, made up with a mirror so as to have about the same weight as nearly as possible as the astatic combination to be examined, was suspended from the fibre in a vibration-box furnished with a long glass tube. The copper ultimately employed was supposed to be electrolytically pure. The combination at first was slightly diamagnetic, but became much less so as the paint-cement dried, and was finally almost indifferent to any means we could find for testing it. From experiments with this disk, whose weight and moment of inertia were known, the coefficient of torsion of the fibre was found to be $T = \cdot 000115$ C.G.S., with a load of ·287 gram.

Two astatic combinations were next mounted and tested. The first was the one that had already done some work in the galvanometer, the second was carefully made for the purpose. The moment of inertia of the first was found to be ·02126, and of the second ·03274.

With both combinations two sorts of experiments were made. The time of vibration of each was determined, and the change of zero produced by twisting the upper end of the fibre through a known angle, generally $2\pi$. From these well-known methods it was found that the systems had a period of vibration of about 2·51 seconds only. This corresponded to a value for the moments of the forces of about ·1270. The magnitude of this number, as well as the positions taken up by the combinations, showed not only that the astaticism was far from perfect, but also indicated the cause of this: the magnets were not really in one plane. Tentative twisting of the aluminium wires was then resorted to, with the result of bringing up the periods of vibration to 11 and 12·8 seconds respectively. In this latter case the moment was reduced to ·0064. The needle that had been brought to a free period of 11 seconds was mounted in the galvanometer, and by means of the controlling magnet was brought to have a period of 36 seconds, corresponding to a magnetic moment

of about ·0007 C.G.S. During the experiments on resistance the period was got considerably longer than 35 seconds.

The next paper, on the Resistance of Impure Sulphur, contains the details of the method employed to find both the specific resistance of the gums mentioned and of sulphur. As no useful result is to be expected from a publication of the long series of experimental numbers obtained in the work on Gums, I refer to the following paper for the description of the *method* employed, since it remained constant throughout.

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## XXXVI. *On Measurements of the Resistance of Imperfectly Purified Sulphur. By* Prof. Richard Threlfall, *and* Arthur Pollock, *Esq.**

The galvanometer having been brought to a state of sensitiveness of 5 scale-divisions for $10^{-11}$ amperes, the measurement of the resistance of the sample of sulphur in question became a tolerably easy matter. The sulphur had been supplied by Messrs. Hopkin and Williams as "precipitated, washed." It looked clean when melted; but on examination turned out to have the following substances existing as impurities:—

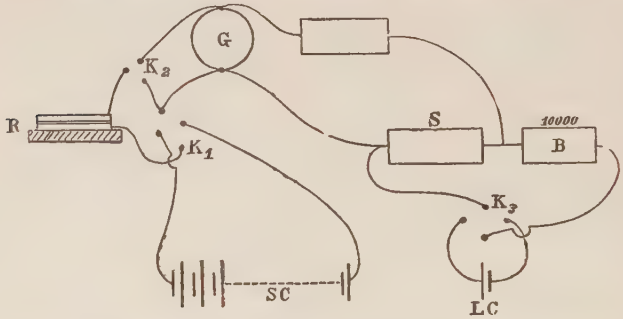
Calcium sulphate.
Ferric oxide.
Organic matter.

Dr. Helms, Demonstrator of Chemistry in the University of Sydney, was kind enough to investigate a sample of this sulphur with a view to discovering whether it contained selenium or tellurium. The result of his examination of about two hundred grammes of the substance was, that neither of these substances was present in quantity large enough to be detected. The examination was carried out by means of the oxidation and sulphurous acid method; and also by the cyanide method. We desire to express our thanks to Dr. Helms. The importance of this result, so far as our work is concerned, lies in the fact that it shows that pure sulphur

* Read March 23, 1889.

can probably be obtained from the sample at hand by means of distillation. The following measurements refer to the unpurified sample; the only substance existing in any considerable quantity was calcium sulphate. The sample was probably rather more pure than ordinary "roll" or flour sulphur. The general arrangement of the apparatus will be clear from the following diagram.

By means of the key $K_1$ a current can be sent in either direction through the resistance R and the galvanometer G. The source of this current is a suitable number of small Clark cells SC. The E.M.F.'s of these cells and of the large one LC were watched during the experiments with the aid of an auxiliary galvanometer and balance arrangement not shown in the diagram. The key $K_2$ allowed the upper metal plate of the resistance arrangement to be put in communication with the last cell so as to charge up without allowing the




current to rush through the galvanometer. After charging, the connexions were altered so as to allow the current due to the leak through the sulphur to pass through the galvanometer. The E.M.F. of the small cells was not changed by this amount of leaking, and the fall of the large cell was measured at the time in the usual manner. The experiment consisted in taking plugs out of the box S till the galvanometer gave the same deflexion whether the current was sent through it by the number of cells through the sulphur, or by the adjustable fraction of the E.M.F. of the large cell through a megohm. The sum of the resistances of S and R was always 10,000 legal ohms. The arrangement of the observations was such that they interlocked in time.

The absolute value of the result, therefore, depends chiefly on the value of the megohm. Respecting this standard I wrote to Messrs. Elliott to inquire what degree of reliance could be placed on it, and was informed in reply that it had been tested against a standard in blocks of 100,000 ohms each, and was right within the variation produced by one degree of temperature. The wire was of German-silver. As the present results are interesting only with respect to the method and the resistances of the sample under varying E.M.F.'s, the absolute value of the megohm is of comparatively small importance.

The following table gives the data of the experiments on the resistance of the sulphur:—

| Date. 1888. | Temperature of room. | No. of small cells used. | E.M.F. of set of small cells. | E.M.F. of large cell short-circuited through 10,000 L. ohms.* |
|---|---|---|---|---|
| | ° | | volts. | volts. |
| Oct. 20 ... | 17·0 C. | 20 | 28·661 | 1·432 |
| 20 ... | 17·0 C. | 40 | 57·312 | 1·432 |
| 21 ... | 16·2 C. | 40 | 57·312 | 1·432 |
| 21 ... | 16·2 C. | 20 | 28·661 | 1·432 |

| Date. 1888. | Resistance taken out of S. | Thickness of layer of sulphur. | Area of layer of sulphur. | Resulting specific resistance of the sulphur. |
|---|---|---|---|---|
| | L. ohms. | centim. | sq. centim. | |
| Oct. 20 ... | 9·0 | 0·05 | 189·8 | $8{\cdot}575\times10^{13}$ l. ohms. |
| 20 ... | 15·0 | 0·05 | 189·8 | $10{\cdot}286\times10^{13}$ „ |
| 21 ... | 10·7 | 0·05 | 189·8 | $13{\cdot}307\times10^{13}$ „ |
| 21 ... | 5·8 | 0·05 | 189·8 | $14{\cdot}425\times10^{13}$ „ |

* Lord Rayleigh has kindly pointed out to us that by a mistake in our method of reduction we have slightly underestimated this value. The result will be that the absolute value of the resistances as given are very slightly too large.

The following is a sample of the readings taken:—

Deflexion of Galvanometer with current from 20 Clark Cells sent through the Sulphur.

| Deflexion. | | Double deflexion. | Zero from deflexion. | Observed zero. |
|---|---|---|---|---|
| Right. | Left. | | | |
| Divs. of scale. | Divisions. | Divisions. | Divisions. | Divisions. |
| +60 | +145 | 85 | +102 | + 95 |
| +50 | +145 | 95 | + 97 | +100 |
| +60 | +148 | 88 | +104 | +100 |
| +70 | +150 | 80 | +110 | +100 |
| +65 | +143 | 78 | +104 | +100 |
| +75 | +150 | 75 | +112 | + 98 |
| +68 | +143 | 75 | +107 | + 98 |
| +70 | +135 | 65 | +102 | + 90 |
| +40 | +135 | 95 | + 87 | + 88 |
| +60 | +140 | 80 | +100 | + 85 |
| +45 | +133 | 88 | + 89 | + 85 |
| +35 | +115 | 80 | + 75 | + 80 |

Deflexion of Galvanometer with fraction of current from large Clark Cell.

| Resistance taken out of S. | Deflexion. | | Double deflexion. | Zero from deflexion. | Observed zero. |
|---|---|---|---|---|---|
| | Right. | Left. | | | |
| L. ohms. | Divisions of scale. | Divisions of scale. | Divisions of scale. | Divisions of scale. | Divisions of scale. |
| 10 | +55 | +150 | 95 | +103 | +105 |
| 9 | +60 | +143 | 83 | +101 | +103 |
| 9 | +60 | +145 | 85 | +101 | +103 |
| 8 | +68 | +140 | 72 | +104 | +103 |
| 8 | +70 | +140 | 70 | +105 | +103 |
| 9 | +60 | +145 | 85 | +101 | +100 |
| 8 | +63 | +130 | 67 | + 96 | + 90 |
| 9 | +50 | +133 | 83 | + 91 | + 90 |
| 9 | +45 | +130 | 95 | + 92 | + 85 |
| 9 | +35 | +120 | 85 | + 77 | + 80 |
| 9 | +35 | +120 | 85 | + 77 | + 80 |
| 8 | +40 | +115 | 75 | + 77 | + 78 |
| 8 | +40 | +115 | 75 | + 77 | + 80 |

Rejecting those observations with the sulphur in which the zero from the deflexions differs from the observed zero by 10 divisions and over, the mean double deflexion with a current from 20 Clark cells sent through the sulphur is 85·5

divisions, and the mean deflexion with the current from the large Clark cell when S = 9 ohms is 85·9 divisions.

The difficulties which had to be met during these measurements seemed to arise from what, following Mr. Bosanquet, we at first called "ghosts." These phantoms, however, seem to have arisen from people opening and shutting doors with iron locks; as a general rule the galvanometer was got properly sensitive overnight, and it was found that if on the following morning the light-spot was where it had been left, then the observations were practically successful; if, on the other hand, the light-spot had gone off the scale, then there was not much use in going on. The disturbance of the fibre consequent on restoring the old zero did not seem to wear itself out under at least twelve hours. It is practically impossible to get a galvanometer of this degree of sensitiveness to work with a silk fibre, the zero being always on the move. In order to get rid of air-currents the ventilators of the room required to be covered up, and the well-made galvanometer-case had to be enclosed in a cardboard box. The insulation at first gave great trouble. It is necessary to support the wires on insulating stands of the paraffin-bottle form, the cells, resistance-boxes, galvanometer, &c. on sheets of glass, themselves resting on small cylinders of paraffin. The insulation of the handles of the keys requires attention. Paraffin keys are much better than ebonite ones.

In pushing the sensitiveness of the galvanometer beyond this point, the following precautions should be observed besides those already mentioned. The arrangement for supporting the magnets should be quite independent of the arrangement for supporting the suspension. The base of the instrument should be of gun-metal and all the framework of metal. The adjustments of the controlling magnets must be capable of being made with extraordinary accuracy. The mirror must be good enough to be used in a telescope. The quartz fibre should be at least six feet long; it must be cemented to its connexions with hard paraffin. The whole apparatus should, we think, be placed in a thick soft iron cylinder, but about this we are not sure. We are tolerably certain, however, that it is in anybody's power to construct a galvanometer on these lines with a sensitiveness of $10^{-13}$

amperes per scale-division and a time of swing of about 40 seconds. Such an instrument, however, could only be used in a tolerably non-magnetic building, and one steady enough to be free from the vibration caused by people walking about. Our best results were got at night and on Sundays, and this in spite of the room having a concrete floor reposing on twenty feet of broken stone and all the instruments being supported on slate benches.

As to the results quoted, no discussion will be given here as we are investigating pure samples of sulphur. It may, however, be mentioned that the resistance depends considerably on the time the current has been flowing, on the electromotive force, and on the temperature.

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## XXXVII. *On a Physical Basis for the Theory of Errors.* *By* CHARLES V. BURTON, *D.Sc.**

1. IN deducing a law of error, two courses seem open to us. We may make our assumptions as general as possible, so that our results shall have the widest application, and shall in the long run approach most nearly to the truth; or we may treat each separate case as a special problem in probability, taking account of all that we know concerning the actual conditions.

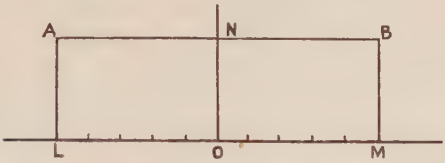
I shall here endeavour to illustrate the latter method by means of some examples; proceeding next to the resultant law of error when two or more elements are combined which are independently subject to error. The most advantageous combination of fallible measures will then be shortly discussed, and, finally, subjective or personal errors will be considered.

2. Suppose that we are given a series of numbers, known correctly to any required number of places, and that from this we write down the same series correct to four places. There will be no uncertainty in the operation unless the digit in the 5th place is 5, and all the remaining digits zero; and (in general) the chance of this occurring is indefinitely small. The limits of possible error are obviously $\pm$·00005, and all errors between these limits are equally probable, unless from

* Read November 1, 1889.

our knowledge of the series we have *à priori* evidence to the contrary. The curve of error (as one may call it) is thus a finite straight line A B (fig. 1), parallel to the axis of errors L M, and bisected by the ordinate of no error, O N. If the original table is carried only to (say) 5 places the case will be somewhat changed. About $\frac{1}{10}$ of the series of numbers will have 5 in the 5th place of decimals; the remaining $\frac{9}{10}$ of the series will all be *correct* to 4 places, and will have errors ranging uniformly between $\pm\cdot000045$. Of the first-

Fig. 1.




named $\frac{1}{10}$ of the series, half will have errors between $+\cdot000045$ and $+\cdot000055$, and half will have errors between $-\cdot000045$ and $-\cdot000055$; the distribution between these limits being uniform*. The corresponding curve of error is given in fig. 2.

Fig. 2.

3. A similar case is the following. Suppose we have to record successive positions of an index upon a fixed scale, which is graduated in centimetres, and that readings are to be taken to the nearest centimetre. If our judgment were infinitely acute, the errors would lie uniformly between $\pm\cdot5$ centim.; but in practice there will also be subjective errors, the consideration of which is left to a later section (§ 10).

4. Next let us consider the error introduced by friction into the equilibrium position of a movable index. Suppose that the index has one degree of freedom, and that if friction

* That is, supposing that ·00005 is added in the case of half of these numbers, and subtracted in the case of the remaining half.

were removed its vibrations would be simple harmonic ; the frictional coefficient being the same at rest and at all speeds. During a half-swing—say to the right—there will be a constant force (or a constant moment) of friction urging the index to the left, and its motion during the half-swing will be harmonic and in the same half-period as if friction were absent, the only difference being that the mean position of the half-swing lies somewhat more to the left. In the return half-swing there will be the same half-period, the mean position being equally displaced to the right. The amplitude is thus decreased by the same amount at each half-swing, until finally a half-swing leaves the index between the limiting positions of friction, where it remains permanently at rest. If the initial displacement (D) of the index was large compared with the range of frictional error ($\pm d$), we may assign the same probability to all displacements between $D-2d$ and $D+2d$ ; and since the final displacement differs from D by an exact multiple of $2d$, it immediately follows that all final displacements between $\pm d$ are equally probable, larger errors being impossible. The curve of error will be like fig. 1.

If friction is greater when the index is at rest, the result is rather curious. Let $\pm d'$ be the limits of equilibrium under statical friction ; then there will be equal probabilities of

Fig. 3.

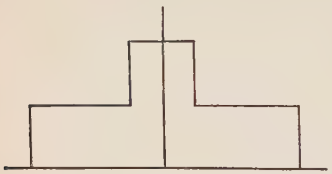


Fig. 4.

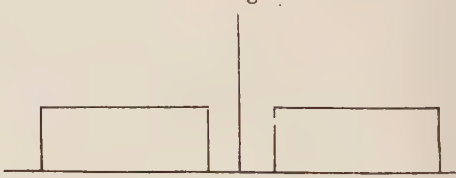


Fig. 5.

errors between the limits $2d-d'$ and $-d'$, and also between $-2d+d'$ and $+d'$. If $d'$ is $<2d$, these ranges of error overlap, and the curve of error is like fig. 3 ; if $d'$ is $>2d$ the curve is like fig. 4 ; if $d'=2d$, we have simply fig. 5.

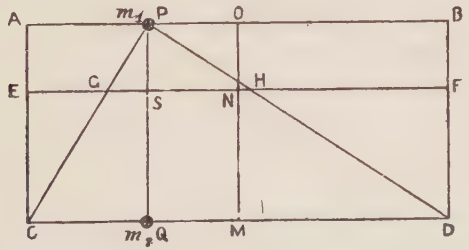
These results are easily obtained by considering initial displacements between the limits $4nd+d'$ and $4(n+1)d+d'$, where $n$ is an integer; they refer of course to the actual, not to the observed, position of the index. If, while the index was in motion, three successive excursions were read (with perfect accuracy), the inferred position of equilibrium would only be subject to an error due to *deviations* from the assumed laws of friction.

5. Now let a declination-needle which is to trace a continuous record be subject to frictional error. If the black line in fig. 6 represent the true declination-curve, the curve traced by the needle will be something like the dotted line. Here the law of error depends on the (variable) friction of the needle, and *on the kind of changes which occur in the quantity measured*; it will further be influenced by the moment of inertia of the needle.

Fig. 6.

6. Enough has now been said to show that the law of error to be adopted depends in some measure on the nature of each special case; we may next consider how to find the law of error when two or more fallible elements are combined. To commence with, take two elements whose curves of error are of the type of fig. 1, the limits of error being $\pm m_1$ and $\pm m_2$ respectively. In the rectangle A C D B (fig. 7), let A O = O B

Fig. 7.




= C M = M D = the unit of length; and let a particle be chosen whose mass is numerically equal to $m_1$. If this particle

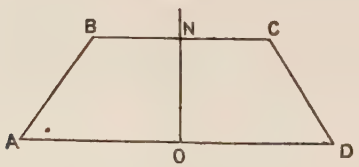
be placed at O P to represent an actual error $= m_1 \mathrm{O\,P}$, it is evident that the *uniform* motion of the particle from A to B represents the distribution of errors between the limits $m_1$OA and $m_1$OB, that is, between $\pm m_1$. The second source of error may be similarly represented by a particle of mass $m_2$ which moves uniformly from C to D. When $m_1$ is at P and $m_2$ at Q, the resultant error will be $m_1\mathrm{OP} + m_2\mathrm{MQ} = (m_1+m_2)\mathrm{NS}$, where S is the centre of mass of $m_1$ and $m_2$.

To form the most general series of combinations, let $m_2$ move backwards and forwards very rapidly between C and D, always with (numerically) the same velocity, while at the same time $m_1$ moves uniformly and very slowly from A to B. By following the movements of the mass-centre along E F, we shall find the law of frequency of the resultant error. Join P C, P D, cutting E F in G and H; then while $m_1$ is passing through P, the mass-centre is moving uniformly between G and H; and as $m_1$ moves from A to B, G H moves uniformly from the position in which G coincides with E, until H coincides with F. The chance of an error lying between $(m_1+m_2)x$ and $(m_1+m_2)(x+\delta x)$ is equal to

$$\frac{\delta x}{\mathrm{GH}} \times \left[\begin{array}{l}\text{Fraction of its time of flight during}\\ \text{which G H includes the element } \delta x.\end{array}\right] \quad . \quad . \quad (1)$$

In general the curve of error will take the form A B C D (fig. 8); where A O = O D = unit length, and abscissæ are

Fig. 8.

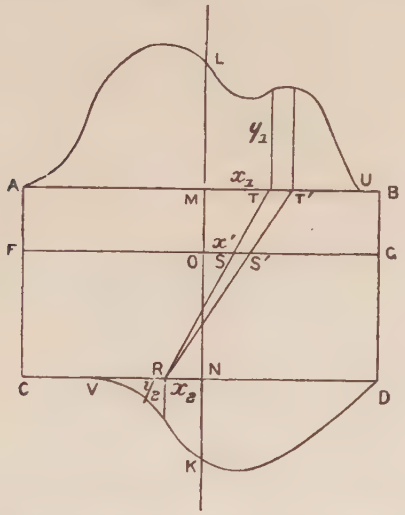



to be multiplied by the constant coefficient $m_1+m_2$. If $m_1=m_2$, B C vanishes, B and C coinciding with N; if $m_1$ and $m_2$ are very unequal, B C preponderates, and A B, D C are nearly vertical.

7. Next to combine two independent sources of error, each following any known law. In the rectangle A B D C (fig. 9) let A M = M B = C N = N D = unit of length. Let the numerical maxima of the errors be $m_1$ and $m_2$, and the curves of

error $y_1=\phi_1(x_1)$ or A L U, and $y_2=\phi_2(x_2)$ or V K D. Following the method of the previous section, let the mass $m_1$

Fig. 9.




move very rapidly backwards and forwards between A and U or between A and B, having at each point of its path a velocity inversely proportional to the corresponding ordinate; (adding U B to the path makes no difference, since the velocity in this part would be infinite). Similarly let $m_2$ move from C to D with a very small velocity, which follows a similar rule. First of all let the mass $m_2$ be passing through R (NR$=x_2$), so that the second error has the value $m_2x_2$; also in fig. 9 let MT$=x_1$, TT$'=\delta x_1$, OS$=x'$, SS$'=\delta x'$. Then the chance of a resultant error between $(m_1+m_2)x'$ and $(m_1+m_2)(x'+\delta x')$ = the chance that $m_1$ is moving between T and T$'$

$$=y_1\delta x_1 \div \text{area ALU};$$

$$=y_1\frac{m_1+m_2}{m_2}\delta x' \div \text{area ALU}.$$

For simplicity, let the scale of ordinates be chosen so that the area ALU = VKD = unity; then the chance that R may lie between $x_2$ and $x_2+dx_2=y_2\,dx_2$.

Hence, taking both movements into account, the chance of

an error between $(m_1+m_2)x'$ and $(m_1+m_2)(x'+dx')$

$$=\frac{m_1+m_2}{m_2}dx'\int y_1 y_2\, dx_2;$$

$y_1$ and $y_2$ being connected by the relation

$$m_1x_1+m_2x_2=(m_1+m_2)x',$$

and the limits of integration being determined by

$$x_1^2<1, \quad x_2^2<1.$$

With similar notation for $n$ independent sources of error, we shall have for the chance of a resultant error between $(m_1+\ldots+m_n)\,x'$ and $(m_1+\ldots+m_n)\,(x'+dx')$

$$dx'\,\frac{(m_1+m_2)(m_1+m_2+m_3)\ldots(m_1+m_2+\ldots+m_n)}{m_2m_3\ldots m_n}$$

$$\times\iint\ldots\int y_1y_2y_3\ldots y_n\,dx_2dx_3\ldots dx_n; \quad . \quad . \quad (2)$$

where $m_1x_1+m_2x_2+\ldots+m_nx_n=(m_1+m_2+\ldots+m_n)x'$, and the limits of integration are given by

$$x_1^2<1,\ x_2^2<1,\ldots x_n^2<1.$$

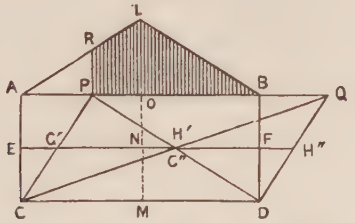
If we make $n$ infinite, each of the $y$'s equal to $\frac{1}{2}$, and all the $m$'s equal, this reduces to the case from whose approximate solution Laplace deduced his law of error.

8. If we follow up the operation of § 6 by successively adding sources of error of the type of fig. 1, we shall find that the resultant curve rapidly approaches the Laplacian form, the discontinuities being continually of a remoter order. Thus with two errors (fig. 8) the curve meets the axis of errors and has only discontinuities of direction; with three errors there are discontinuities of curvature, and so on. The curve produced by combining $n$ errors of this type will have contacts of the $(n-2)$th order with the axis of errors; and the resultant of two curves with contacts of the $m$th and $n$th orders respectively has contacts of the $(n+m+2)$th order; for contacts of the $m$th and $n$th orders would be produced by combining $m+2$ and $n+2$ errors respectively.

To illustrate these principles, consider the error introduced into the indications of a balance by the friction of its knife-edges; and to simplify the case, suppose that the balance is allowed to come to rest before a reading is taken. We are only concerned here with errors in the *actual position* of the

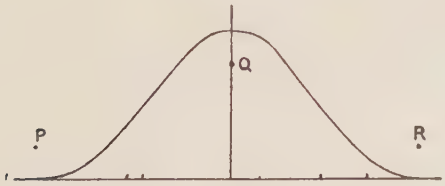
pointer, supposing the weights correct and the balance just. The friction at each knife-edge is a source of error, and the three sources of error are (at least very approximately) independent. Let the frictional coefficient at each knife-edge be constant, the maximum error due to the central knife-edge being double that due to either of the others; there are then three curves of errors of the type of fig. 1. The two equal sources of error being compounded will give the curve A L B (fig. 10), whose maximum error is equal to

Fig. 10.




the maximum value of the remaining error. We shall thus have two equal masses, one moving rapidly backwards and forwards along C D with numerically constant velocity; the other moving slowly from A to B with a slowness proportional to the corresponding ordinate; and the expression (1) will evidently be applicable. Consider an element $\delta x$ at H; then the second factor of (1) = chance that the slowly-moving mass lies between P and Q = the area P R L B. As H′ moves from E to F, P Q moves from the position in which Q coincides with A, until P coincides with B. The resultant curve of error will consist of three arcs of equal parabolas (fig. 11) with foci at P, Q, and R. For deter-

Fig. 11.




minations by the method of double weighing, we must compound this curve with another equal and similar curve.

9. *Most advantageous combination.*—Suppose we have a number ($n$) of independent measurements ($a_1, a_2, \ldots a_n$) of the same quantity. Let the chance of an error between $x_1$ and $x_1 + dx_1$ in $a_1$ be

$$\frac{1}{c_1\sqrt{\pi}} \cdot e^{-\phi_1(x_1)}\, dx_1, \quad \ldots\ldots\ldots (3)$$

with similar notation for the remaining measures—an assumption which is perfectly general. By adopting X as the *true* value we assume the errors in the respective measures to be

$$(a_1 - X),\ (a_2 - X), \ldots (a_n - X).$$

If we know the limits of *possible* error for one of the measures, $a_r$, then $a_r - X$ must be made to fall within these limits. Subject to such restrictions we must make the product

$$\frac{1}{c_1\sqrt{\pi}} \cdot e^{-\phi_1(a_1-X)} \frac{1}{c_2\sqrt{\pi}} e^{-\phi_2(a_2-X)} \cdots \frac{1}{c_n\sqrt{\pi}} \cdot e^{-\phi_n(a_n-X)}$$

a maximum; that is we must make

$$\phi_1(a_1 - X) + \phi_2(a_2 - X) + \ldots + \phi_n(a_n - X) \text{ a minimum}. \quad (4)$$

If Laplace's law of error applies to each of the independent measures, then

$$\phi_1(a_1 - X) = \frac{(a_1 - X)^2}{C_1^2}, \ \ldots . \phi_n(a_n - X) = \frac{(a_n - X)^2}{C_n^2};$$

and (4) reduces to the method of least squares. We can also see from (4) how the most advantageous combination of measures depends on the laws of error in the separate observations; and that Laplace's law of error alone leads to the method of least squares.

As another particular case, let each of the quantities $\phi_1(x_1)$, $\phi_2(x_2) \ldots \phi_n(x_n)$ be constant between certain limits, and possible only between those limits; this will in general give a finite possible range to the value of X, all values within this range being equally probable.

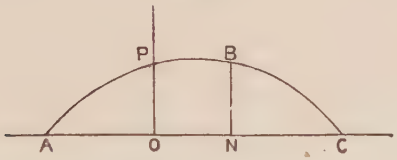
The method of finding the most advantageous combination of measures by making the probability of the assumed value a maximum was given by James Ivory*; it appears to me the most direct and satisfactory, and indeed the only method which is applicable in all cases. The intimate relation which

* Phil. Mag. 1825, vol. lxv. pp. 161 *et seq.*

has here been shown to exist between Laplace's law of error and the method of least squares is also in agreement with the results somewhat differently deduced in Ivory's paper.

10. *Subjective errors* remain to be considered. Suppose that in § 3, when the index is nearly halfway between two graduations, we may not decide correctly to which graduation it is nearest. Let A B C (fig. 12) represent the curve of

Fig. 12.




error when the observer attempts to place this particular index halfway between two graduations, O P being the ordinate of no error; so that O C and O A represent the limits of error. Now if the distance of the index from a graduation lies between +·5 centim. −OC and −·5 centim. −OA, its position will be taken as certainly nearer to that graduation than to any other, and the corresponding errors for such positions of the index will be uniformly distributed between these limits. Draw any ordinate B N of the curve A B C; then the chance that in trying for the middle of a division we should *discard the position* N *for one more to the right*

$$= \text{area N B C} \div \text{area A B C}; \quad . \quad . \quad . \quad . \quad (5)$$

when N is to the left of A, this chance becomes a certainty. The curve of error, then, for readings to the nearest centimetre will be straight and horizontal in the middle, the terminal portions being found by integrating A B C from A to C and from C to A.

11. This method of treatment is not free from assumption; it would only be strictly applicable if our judgment were on each occasion perfectly definite and decided, but at the same time subject to a variable error following a known law of frequency—like the definite but fallible indications of a physical index. But it is evident that when an index is sufficiently near to its true position (or to our more or less biased conception of its true position), we shall have no choice

in saying in which direction the error lies, and therefore no motive in altering the adjustment. Now the bias and want of acuteness of our judgment will of course be variable, the circumstances which affect them (experience, fatigue, illumination, &c.) being almost endless; but I think this principle may be conceded: *If an index be placed in a given position and examined from a given point of view, we shall judge the adjustment to be correct when, but not unless, the error falls between certain limits; such limits being determined by subjective and other conditions at the time of the observation.*

12. Now consider (merely for the sake of illustration) two ways in which an adjustment may be made. Suppose we are measuring the positions of spectrum-lines by bringing a wire into coincidence with them, and disregarding parallactic and instrumental errors, let us confine our attention to errors of judgment in adjusting the cross-wire. First let the determinations be made in this (impracticable) manner: the micrometer-head is first moved at random, and then the field observed, and if, in the judgment of the observer, the vertical wire coincides accurately with a spectrum-line, the micrometer reading is recorded. Whenever an apparent coincidence is registered, the error of judgment must have fallen between certain limits; and obviously it is equally likely to have any value between those limits. In a number of observations the law of error may be determined as follows:—Draw a number of horizontal lines (fig. 13) each representing on a convenient scale the limits of possible error at the time of an observation*. The relative frequency of an error O N will be proportional to the number of horizontal lines cut by the ordinate P N. In general the curve of error for a large number of observations will be straight and horizontal in the middle, falling down towards the ends so as to meet the axis of errors; if the limits of errors of judgment were invariable, the curve of error would be of the type of fig. 1.

Fig. 13.

13. Perhaps in practice we shall more nearly approximate to the following plan:—Starting with the wire in a position

* What we really require to know is the *law of frequency* for the *limits* of error.

which is evidently in error, we shall move it up to the spectrum-line until no further error can be detected. If we really stop moving the wire as soon as we cease to feel a distinct motive for doing so, we shall be just at the limit of possible error corresponding to that time. For a series of *single* observations the curve of error would perhaps be something like fig. 14.

Fig. 14.

14. As a final example, suppose we are trying to place a small round body in a given position in a plane. Here the law of error will depend on our manner of testing the adjustment: whether we merely look up and down and from side to side to get two (very nearly independent) judgments of the corresponding coordinates, or whether we examine the object from every point of view to make sure that no error can be detected. The case may be illustrated mechanically by supposing two pendulums supported one on gimbals, the other after the manner of Foucault's pendulum; appropriate laws of friction being assumed. The law of error will further depend on whether we follow the method of § 12 or of § 13.

If we were trying to drive a billiard ball from one given position so as to make it come to rest in another given position (without rebounds), the errors of direction and of distance would, if small, be very nearly independent; the latter coordinate being probably subject to much greater variation.

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We are led, then, to the following conclusions:—The law of error in a set of observations depends on the nature of each special case; and what may be called the probable law of error is determined by our knowledge of the conditions. The combination of three or more sources of error of comparable importance gives in general a law of frequency not seriously differing from that of Laplace; so that the method of least squares will be practically the most advantageous, except where a single source of error with a very different law is predominant above all the rest.

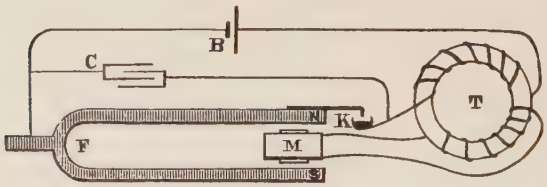
## XXXVIII. *On a Method of Driving Tuning-Forks Electrically.* *By* W. G. Gregory, *M.A., Demonstrator in Physics at the Royal Indian Engineering College, Coopers Hill**.

In the ordinary method of driving tuning-forks by electricity, the battery circuit is completed just before the end of the stroke and broken again soon after the commencement of the return motion. Thus the fork receives its impulse at a most unfavourable moment, *i. e.* when it is stationary. The impulse can be considerably delayed by including in the battery circuit a solenoid into which a solid iron core is inserted more or less till the best result is obtained. This adjustment, however, varies with the amplitude of vibration and the alterations of the contact. The whole matter was discussed in a paper read before the Physical Society on June 26th, 1886, by Prof. S. P. Thompson†, who then suggested the employment of two similar forks which drove one another and settled down to a difference of phase of a quarter of a period. Each fork, therefore, received an impulse when moving at its greatest velocity in the middle of its stroke.

The method I now suggest accomplishes the same thing without the employment of a second fork, and moreover gives two impulses in each complete period instead of one.

The arrangement is shown in fig. 1.

Fig. 1.




F is a tuning-fork mounted in the usual way, and provided with a driving electromagnet M, and contact-maker K. But instead of taking the main battery-current directly through the electromagnet M, it is sent through the primary coil of a kind of transformer T, the secondary circuit of which is

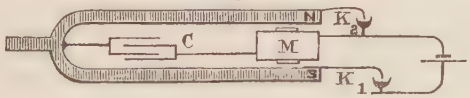
* Read November 1, 1889.

† Proc. Phys. Soc. viii. pt. ii. ; Phil. Mag. [5] xxii. p. 216.

connected to the electromagnet. Hence, at both make and break of the main circuit, momentary induced currents pass through the driving magnet alternately in opposite directions. By polarizing the fork so as to make it a horseshoe-magnet, the impulses are also made to act alternately as attractions and repulsions, and the fork receives two impulses for each complete vibration. By properly adjusting the contact when the fork is at rest, so as just to complete the circuit, the impulses will be given very approximately at the middle of the stroke, and are independent of the amplitude of vibration. The fork I tried made about 86 vibrations per second, and had prongs 20 cms. long and 1·8 cm. apart. The electromagnet M was formed by winding about 50 turns of no. 22 silk-covered copper wire round a core formed of a bundle of varnished iron wire. It was mounted on a wooden support capable of sliding between and parallel to the prongs. The transformer T consists of a core of cotton-covered iron bonnet-wire wound in the form of an anchor-ring having a mean diameter of 6 cms. and thickness 1 cm. Round this is wound the secondary coil of about 160 turns of no. 22 silk-covered copper wire, forming a single layer completely round, and outside this the primary of about 190 turns of similar wire. A condenser C of 4 microfarads capacity was connected across the mercury-break K to diminish the sparking. One small accumulator B sufficed to work the fork vigorously, the mean current consumed being about 2 amperes. By increasing the number of turns of wire, much less current would be required, but there would be a limit, since the lag must not be so great as to interfere with the proper timing of the impulses.

An alternative method, using far less current but requiring two contacts, is shown in fig. 2.

Fig. 2.




The contact $K_1$ charges the condenser C and $K_2$ discharges it. The currents of charge and discharge are both taken through the electromagnet M, and the action is the same as above, the fork being, of course, polarized. It would be

necessary to wind the magnet M with many turns of wire, to use a battery of high E.M.F. and a large condenser. The latter, however, could probably be replaced by a polarizable battery of platinum or lead wires in dilute sulphuric acid. Except for economy of working, it is not so good a method as the first, as the adjustments of the contacts $K_1$ and $K_2$ must be very exact.

As regards magnetizing the fork, there can be no real objection to that, for in the usual method of driving it soon acquires a polarity. In fact the fork I first tried worked at once without any further magnetization.

Prof. S. P. Thompson said the methods, if perfect, would be of great service, and suggested that a fork so driven be tested optically by comparison with a freely vibrating one. He regarded the mercury-contacts used as objectionable, for their capillarity and adhesion would probably cause the impulses to lag behind the appointed epochs.

Prof. McLeod remarked that Lissajou's Figures gave a satisfactory method of testing the constancy of period, and could be readily observed without using lenses; and in reference to liquid condensers suggested by the author for his second device, said that platinum plates in sulphuric acid were found to disintegrate when used for this purpose. He thought lead plates would prove suitable.

Prof. Jones, who read a paper on a similar subject in March last, said he now used bowed forks with which to synchronize the speed of the disk there described, and the frequency is determined by causing the disk to complete the circuit of his Morse Receiver once each revolution.

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## XXXIX. *On a New Electric Radiation Meter. (Preliminary Note.)* *By* W. G. Gregory, *M.A., Demonstrator in Physics at the Royal Indian Engineering College, Coopers Hill**.

The usual method of detecting electric radiations by observing the sparking across an air-gap in the wire used as a receiver admits of only a rough estimate of their intensity.

* Read November 1, 1889.

The object of this paper is to describe an instrument by means of which definite quantitative measurements may be made. It is based on the measurement of the elongation of a wire when heated by the currents induced in it by the rapidly varying field of force.

It consists of a long glass tube A B cemented to a shorter piece of brass tubing B D. Within is stretched a platinum wire W fastened to the glass tube at A and to a Perry magnifying-spring at M, where there is a mirror to indicate the rotation of the spring by the reflexion of a beam of light upon a scale. At E there is a nut and screw for adjusting the tension. The brass tube is partially filed away in front of the mirror to form a window. The object of the brass tube is to compensate the spring for general changes of temperature, the glass tube serving the same purpose for the platinum wire.

The wire employed was ·0086 cm. in diameter, and 192 cms. long. The spring was about 25 cms. long and ·007 cm. in diameter. It was made out of a fine kind of tinsel ·04 cm. wide and ·0015 cm. thick, which can be obtained at fancy shops wound loosely on cotton. When removed from the cotton, it was already in the form of an irregular helix. It was then rolled tightly between the fingers to reduce the diameter as much as possible. A piece of silk was next attached to one end, and the spring extended almost to breaking-point, the silk allowing it freely to untwist as much as it would. After this it was rolled between two hard surfaces and again pulled out. This was repeated till at last 10 revolutions per millimetre extension were obtained.

The mirror was a $\frac{2}{10}$-inch worked concave one, and gave a very sharp image of a wire on a scale one metre off. Using an ordinary galvanometer-scale, it was easy to read to one division. This would correspond to an elongation of the wire of ·000005 of a millimetre, and a rise of temperature about ·003 of a degree Centigrade. In spite of this sensitiveness, only one or two divisions' deflexion were obtained with the oscillator 4 metres off. The oscillator used consisted of two

brass rods ·53 cm. in diameter supported horizontally and carrying two zinc plates 40 cm. square, capable of sliding along them so that the wave-length could be altered at pleasure. They were usually kept about 25 cm. apart. The terminal knobs were 2 cm. in diameter and the spark-gap about 2 or 3 millim. It was noticed that one of the knobs blackened very quickly but remained quite cool, while the other, which altered little, became very hot.

The induction-coil employed to work it was 20 cm. long and 12 cm. diameter, and gave with the battery-power employed sparks 4 cm. long between two points. To obtain greater regularity in the working of the coil, a tuning-fork mercury break, vibrating 86 times a second, was used.

By employing a larger coil larger deflexions could, no doubt, be obtained and effects at greater distances observed.

A method was tried for increasing the sensitiveness by weighting the mirror so that its centre of gravity was behind and rather above the axis of suspension. The tension was adjusted so that the spring kept the mirror near its position of unstable equilibrium. The effect was to render the smaller deflexions nearly 10 times as great, while the sensitiveness diminished as the deflexions became larger. But the difficulties of working with it were greatly increased, as the smallest draught of air would alter the zero-point.

Wires of different materials were also tried which should theoretically give better results; but, probably owing to their diameters not being sufficiently fine for the tension to which they were subjected, the results were not satisfactory. The convenience of being able to compensate the platinum wire by the glass tube seems, however, a great point in favour of the use of platinum, and has led me hitherto to keep to it.

Prof. Perry asked if the E.M.F. required to produce the observed results had been calculated; he also believed that the sensibility might be increased by using copper instead of platinum, and replacing the spring by a twisted strip.

Mr. Blakesley inquired whether the effect of increasing the capacity of the ends of the wire had been tried.

Mr. Boys said that if the observed effect was due to rise of temperature he would like to see it measured thermally. He

also thought the effect might be due to extension caused by rapid electric oscillations in some such way as the elongation of an iron bar caused by magnetization. In answer to this, Prof. S. P. Thompson said the matter had been investigated experimentally, but with negative results.

Prof. Herschel suggested the use of a compound spring such as are used in Bregnet's Metallic Thermometers.

In reply Mr. Gregory said he had estimated the E.M.F. by observing that a Leclanché cell through 50 ohms produced about the same result. No improvement in sensitiveness was obtained by using copper wire or by increasing its capacity, and attempts to measure the rise of temperature by an air-thermometer had been given up as hopeless.

The President, in thanking the author for his paper, congratulated him on the ingenuity and courage displayed in producing an apparatus to measure such microscopic quantities as are here involved.

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## XL. *On Electrifications due to the Contact of Gases with Liquids.* *By* J. ENRIGHT, *B.Sc.**

A STUDY of Helmholtz's theory of atomic charges led to the experiments I am about to describe. When one has got the idea that molecules are kept in their integrity by the mutual attractions of the oppositely charged atoms or radicals composing them, a question soon arises as to what part, if any, these charges play in ordinary chemical reactions. The theory precludes any other form of chemical affinity than that due to the mutual attractions of the opposite charges, and it occurred to me that since at the moment of reaction there must be disturbance and re-arrangement of them, some indication of their existence might be obtained by allowing reactions to go on in an insulated vessel properly connected with a quadrant-electrometer. Even if a permanent electrification could not follow, I thought it just possible that a momentary flutter of the "spot" might take place on account of the electric disturbance due to the interchange of the charged ions.

* Read November 15, 1889.

This consideration alone was sufficient to excite one to experiment, but if I tell the whole story I must say that I had had other expectations. According to theory the charges on monads are exactly equal. How then does it happen, if reactions be a result of the charges, that chlorine drives iodine out of potassic iodide? How, indeed, does it happen that any one molecule composed of a particular pair of monad elements is stronger,—that is to say, more stable than any other molecule composed of any other pair of monads? And so on. After pondering on such questions for some time, I could not suppress the thought that after all perhaps the charges might not be equal, and that the experiments I had determined to carry out might possibly throw some light on the matter.

Then there were certain special reactions which appeared to afford an admirable opportunity for experimental study of the theory. I refer to cases in which the atomicity of elements undergoes a change during a reaction,

$$2Fe^{II}SO_4 + H_2SO_4 + Cl_2 = Fe_2^{IV}(SO_4)_3 + 2HCl \text{ (Roscoe)}.$$

Here four monad charges of positive electricity attached to the iron on the left change into eight monad charges on the same quantity of iron on the right. If the increment of positive electricity be produced by contact an equal charge of negative ought to be set free, and this ought to be easily detected by the electrometer.

On the whole there appeared, to a strong believer in the theory, a fair and inviting field for experiment. My plan was to examine in the manner indicated instances of the four following types of chemical change :—

(1) Combination of elements.
(2) Displacement.
(3) Double decomposition.
(4) Change of valency.

I may as well say at once that from (3) and (4) I got no result whatever, from (1) only an electrification of little importance, and that it was from (2)—instances of displacement—that the results I wish to call attention to were obtained.

The electrometer was made rather sensitive. A high-resistance Daniell through which a current never passed gave

a deflexion of 94 divisions either way. An insulated plate on which the reactions were to proceed was fixed so that it could be connected or disconnected at pleasure with the insulated pair of quadrants. The insulation of this plate was tested by giving to it a small charge, and connecting it then with the quadrants. The spot moved and came to rest 200 divisions from zero. It was watched for 3 minutes, during which it maintained its position.

A porcelain dish containing about 20 c. c. of a strong solution of potassic iodide was placed on the insulated plate. About the same volume of a strong solution of chlorine in water was placed in a beaker to which was attached a handle of insulating material, and by means of this handle the chlorine water was poured into the potassic iodide. A heavy brown precipitate appeared. The insulated plate was now connected to the insulated quadrants. No deflexion resulted. The experiment was repeated without producing a movement of the spot.

The porcelain dish was now half filled with distilled water, placed on the insulated stand, and a fragment of potassium cast into it. The usual reaction ensued and the "spot" moved 160 divisions to the left, came to rest, and maintained its position. The quadrants were short-circuited, and the spot returned to within 2 divisions of zero.

At first view this appeared exactly what I had expected to occur. On reflection, however, many possibilities suggested themselves and each had to be considered. Had I merely detected electricity in the air? May not the deflexion be due to the inductive action of the charged needle on the quadrants? Was the escaping hydrogen electrified, and if so what was the sign of the charge? I proceeded to repeat the experiment.

The quadrants were short-circuited, and the insulated dish, after being momentarily put to earth, was, as before, connected to the insulated quadrants. A second fragment of potassium was tossed into the water in the dish. The spot moved 28 divisions to the left, then turned and moved up the scale to the right, coming to rest at 200 divisions from zero. The quadrants were once more short-circuited, and the experiment again repeated. The spot moved 40 divisions to the

right. I could not possibly explain such irregular behaviour. I carefully looked up the connexions and tested the instrument. It was in good order. I again repeated, but with similar results.

Sodium was used instead of potassium, and although the deflexions with it were also irregular, the tabulated results showed a contrast. When sodium was used, 40 per cent. of the deflexions were first to the left; when potassium was used, 70 per cent. were first to the left. Speaking broadly, this seemed to indicate that when potassium was used the dish received a negative charge, when sodium was used the dish took a positive charge ; and as I fancied that such a result would enable me to set up some theory with regard to the atomic charges, I tried very hard to eliminate what I then believed to be accidental exceptions and to prove that in reality such was the case.

The porcelain dish was replaced (1) by a glass beaker, and (2) by a metallic dish, the experiment being repeated in every other particular, but without obtaining greater regularity in the deflexions.

I wish to remark here that the method of testing the electrification by keeping the insulated vessel from which gas is escaping in connexion with the insulated quadrants during the reaction is faulty, inasmuch as that under the circumstances a deflexion may be caused by the inductive action of the charged needle on the quadrants. It has, however, this great advantage, viz., that one can see distinctly every variation that may take place during any interval. It will be noticed that throughout the inquiry I use this method for preliminary testing, and that I conclude nothing until I verify by the more rigid process of allowing the reaction to go on while the insulated plate is disconnected from the quadrants, and testing the electrification at its close.

Having failed to get a definite and constant result with water, I proceeded to try other liquids. Sodium and dilute sulphuric acid, sodium and nitric acid, and many other such combinations were tried, and eventually I found that sodium and strong acetic acid gave an *invariable* result, viz., a positive charge on the dish in which the reaction took place. This has not failed hitherto in a single instance.

I reviewed the state of affairs. The first thing to do, as it appeared to me, was to ascertain whether or not the hydrogen carried a charge, and, if so, to determine its sign. I found it so difficult to work with sodium that after many unsatisfactory attempts I decided to search for another metal which would give a similar constant and definite result. One naturally turned to zinc.

A piece of zinc was thrown into dilute sulphuric acid which was put into the insulated dish, the connexions being as already described. The spot rapidly moved 36 divisions to the left, turned, went back across zero and up on the other side 120 divisions. This was not encouraging. It seemed to be the beginning of another set of irregular deflexions. It, however, went to show that electrification was an accompaniment of most chemical reactions. I repeated the experiment several times, varying the degree of dilution of the acid, but failed *then* to get constant results. I next tried hydrochloric acid.

A small portion was placed in the insulated dish and a particle of zinc thrown into it. The spot rapidly moved off the scale to the left, indicating a negative charge on the dish. The quadrants were short-circuited, and the spot returned to zero. Repetition was followed by the same result, and fortunately this turned out to be as constant a deflexion to the left as that from sodium and acetic acid was to the right, while it was much greater in quantity.

I now concentrated my attention on zinc and hydrochloric acid. In this experiment, as in all others where a gas escaped into the air, it was possible, though not likely, that the resulting deflexions were due to atmospheric electricity, and I thought it as well to settle this point at once. A piece of sponge was saturated with alcohol and placed on the insulated plates. It was then fired, and burned with a large flame. The insulated plate was connected to the quadrants when the sponge ceased to burn, and the spot at once moved 10 divisions to the right, indicating a small positive charge on the plate. The experiment was repeated in every particular except the burning of the sponge, but with the result of only a disturbance of the spot of a few divisions.

The air in the neighbourhood of the insulated plate

appeared to be slightly electrified, but as it was of opposite sign to the charge produced by the action of zinc and hydrochloric acid, it was certain that the latter was not due to any atmospheric cause. But a new point of great importance had arisen. Whence came the positive charge in the air near the instrument? The idea of its being due to the evolved hydrogen at once suggested itself. For some time before testing with the sponge, I had been repeating the experiment with zinc and hydrochloric acid in order to satisfy myself as to its constancy, and a considerable quantity of hydrogen had escaped into the air.

The charge on the evolved hydrogen opposite in sign to that on the insulated generator! If this were really the case I saw that I should have to give up certain ideas which I had been fostering while dealing with these experiments. The point had to be at once cleared up.

A zinc goblet was metallically attached, mouth downwards, to the insulated plate. A long-necked flask containing zinc and hydrochloric acid was placed underneath in such position that the hydrogen found its way into the inverted goblet. In two minutes after so placing the hydrogen generator the goblet was tested by connecting it with the insulated quadrants. The spot moved 78 divisions to the right, indicating that the hydrogen escaped with a positive charge—that is to say, as already suspected, its charge was opposite in sign to the acid and generator from which it was evolved.

The experiment was several times repeated, and always with the same result, but it was noticeable that the positive charge on the hydrogen was much less in quantity than the negative charge on the generator. If they were in reality oppositely charged, the quantities, as in all such cases, would be exactly equal. I urged, in explanation, that the hydrogen moving over the moist glass of the long-necked generator must lose some of its charge. However, a confirmatory experiment was devised.

A second insulated plate was set up and connected metallically with the first. A hydrogen generator, containing zinc and hydrochloric acid, was placed on one, and a suitable pneumatic trough was placed on the other, in such manner that the gas might be generated and collected on the insulated

plates, which were connected to the insulated quadrants. A stream of hydrogen was allowed to pass, and by means of an insulating rod the delivery-tube could be placed so that the hydrogen might get into the air or be collected and retained on the insulated plates at pleasure. It was found that as long as the gas did not escape the spot remained motionless, but that when it escaped from the plates into the air the spot moved. This, I took it, proved that the charges on the generator and evolved gas were equal in quantity, though opposite in sign.

The state of the case was now, so far, pretty clear. When hydrogen was produced by zinc and hydrochloric acid the hydrogen became positively, the generator negatively, charged. I set this fact up before my mind and examined it as carefully as I could on every side. I turned it round and round, looking for some information as to the atomic charges, but I could find none. Had the charge on the escaping gas been of the same sign as that on the generator, I could have set up some hypothesis concerning them, but, as things were, nothing of the kind was possible.

But what is the cause of this undoubted electrification? I repeated the experiment many times. I varied the quantities of acid and zinc, and noticed that with weaker acid or a larger quantity of zinc the deflexions were not so strong. During these repetitions I was in the habit of short-circuiting the quadrants when the spot came to the end of the scale, lest the suspending fibres of the needle should get a *set* from being twisted too much in one direction. On one occasion, however, being called away suddenly, I neglected to do so, and the electrification worked its will, so to speak, on the needle. On returning in about twenty minutes, I found that all the zinc was dissolved, and to my very great astonishment the spot was at rest at the extreme right of the scale.

Up to that time the deflexion from zinc and hydrochloric acid had been to the left; and, as I had made the experiment a great many times with this unvarying result, I was much perplexed. The uncertain behaviour of sodium and potassium was still fresh in my memory.

However, what to do on the occasion was quite clear: I

repeated the experiment in every particular, sat down, and watched it. The spot went rapidly off the scale to the left as usual. The reaction proceeded. In eleven minutes the spot appeared again on the scale, went down 100 divisions rather slowly, then more rapidly, crossed the zero, and at a good pace went up the other side almost to the end of the scale. This was quite a new development. Frequent repetition, with the same result, proved that this behaviour, strange as it was, had a definite cause. I varied the strength of the acid and the quantity of zinc, and found that by either making the acid weak or increasing the quantity of zinc I could hasten the reversal of the sign of the electrification of the generator.

I now concentrated my attention on this reversal of sign. I contrasted all the circumstances attending the deflexion to the left with all those attending the deflexion to the right, and could detect only one difference, and that was the production of chloride of zinc in the generator, and I could not fail to see that as the quantity of this salt increased the deflexions to the right became stronger.

From this change of sign of the generator, when a certain quantity of chloride of zinc got into solution, there suddenly appeared to come a ray of light which I thought dispelled the fog which hung round the earlier experiments. The nature of the liquid through which the hydrogen passed apparently determined the sign of the electrification. I paused again to review the events of my little enterprise.

I set out in quest of some direct evidence as to the atomic charges. I had tried the four types of chemical change. From double decomposition and from cases of change of valency I had got no result whatever. From direct union of elements—from the combination of phosphorus and iodine, accompanied by a cloud of $P_2O_5$, and, I suppose, iodine vapour —I had got an electrification. From many cases of displacement I had got considerable electrifications; but from some, such as the displacement of iodine by chlorine, I had got nothing whatever. A careful examination of these results disclosed the fact that no electrification was obtained except when something escaped from the vessel in which the reaction occurred. This circumstance I thought could not

fail to have some meaning. Then there were the leading incidents, as I considered, of the inquiry:—(1) The escaping gases or vapours came off with a charge opposite in sign but equal in quantity to that on the generator. (2) The reversal of the sign of both generator and escaping gas when the liquid in the generator underwent a definite change.

Such were the facts to be brought under some theory. I was reluctantly compelled to conclude that they had nothing to do with atomic charges, but for all that they afforded food for the most delightful contemplations, often for hours at a stretch, during the last two or three years.

Reflect as I may on the reversal of sign of the electrification when a certain quantity of chloride of zinc gets into solution, I can find no explanation for it but the electricity of contact. Hydrogen is positive to hydrochloric acid, but negative to chloride of zinc. And, indeed, looking at the whole matter in this light, from my present standpoint, I can perceive how, in the earlier experiments, the nature of the liquid through which the hydrogen passed decided the sign of the electrification. From hydrochloric acid it was positive; from acetic acid (or it may be acetate of sodium) it was negative. Even the very whimsical deflexions from sodium and water become intelligible. As a piece of sodium careers about on the surface of water, the escaping hydrogen is one instant in contact with water, the next with caustic soda, the next with the side of the vessel, and, accordingly, on the theory of contact, the irregular deflexions are at once explained.

In most of the experiments described above, the hydrogen was allowed to escape from an open dish or beaker, and not from a narrow delivery-tube, for it was found that the gas partially discharged itself when it passed through narrow openings. Whatever tended to electrically connect the charged liquid with the oppositely charged escaping gas, also tended to lessen the charges on both. And besides this, there was the possibility that the contact of the gas with the delivery-tube might cause electrification. On the whole, it was found least ambiguous to half fill an evaporating-dish about 6 inches in diameter and 2 inches high with HCl and drop into it a few fragments of zinc. The bubbles of gas then shot straight up through the middle of the liquid, and passed into

the air without coming into contact with anything else. It was, however, a defect of this mode of proceeding that particles of the acid were projected about in all directions, sometimes beyond the dish. In order to get rid of any doubts on this head, a smaller dish was used and placed at the bottom of a beaker 7 inches high. I propose to give in detail one of several experiments made in this way with all possible care.

The electrometer was *not* in a very sensitive state. The high-resistance Daniell gave a deflexion of 38 divisions on either side. A glass beaker 7 inches high and 5 inches in diameter was placed on the insulated plate. A porcelain dish, $2\frac{3}{4}$ inches in diameter and $1\frac{1}{8}$ inch high, was nearly filled with a 10-per-cent. solution of HCl in distilled water, and placed at the bottom of the beaker just mentioned. Three small fragments of zinc were now dropped into the dilute acid in the small dish. A very slight effervescence at once appeared, and it gradually increased, but never became violent. No trace of spray could be detected at the end of the experiment above the lower half of the beaker. In 4 minutes from dropping the zinc, the spot could be perceived moving, and in $4\frac{1}{2}$ minutes more it had moved 28 divisions to the left, indicating the charge on the dish negative. I append the notes taken during the time the experiment lasted

| | Time. | | Reading. |
|---|---|---|---|
| | h | m | |
| Zinc dropped into acid. Insulated quads connected to insulated generator | 2 | 10 | 378 (zero) |
| Spot moving to left. Generator positive | 2 | 14 | 377 |
| Spot moving faster | 2 | 16 | 367 |
| | 2 | 17 | 360 |
| Insulated quads and insulated generator disconnected | 2 | $18\frac{1}{2}$ | 349 |
| | 2 | $19\frac{1}{2}$ | 349 |
| Insulated quads and generator reconnected | 2 | 20 | 329 |
| | 2 | 21 | 322 |
| Spot stops and appears to return | 2 | $21\frac{1}{2}$ | 319 |
| | 2 | 23 | 328 |
| | 2 | 25 | 346 |
| | 2 | 26 | 366 |
| Spot crossed zero | 2 | $26\frac{1}{2}$ | 378 |
| | 2 | 28 | 388 |
| Quads and generator disconnected | 2 | $31\frac{1}{2}$ | 458 |
| | 2 | 33 | 458 |
| Quads and generator reconnected | 2 | $33\frac{1}{2}$ | 513 |
| Effervescence gets less | 2 | 35 | 550 |
| | 2 | 37 | 562 |
| | 2 | 40 | 568 |
| Quads short-circuited | 2 | 42 | 382 (zero) |

It may yet be urged that when hydrogen passes through hydrochloric acid, it carries with it both HCl gas and vapour of water, and that the electrification is due to these, and not to the hydrogen. In order to test the suggestion, I placed on the insulated plate a dish nearly filled with boiling concentrated HCl. In two minutes the plate was connected with the insulated quads, but the spot moved only 1 or 2 divisions. It was then watched for more than 5 minutes, but the spot did not stir although clouds of vapour were escaping from the acid.

I cannot help remarking on the difficulty of neutralizing a gas—at all events, hydrogen. The following experiment is well calculated to illustrate this properly, while it affords, I submit, a very stringent verification of the experiment to which the notes are appended. The large beaker with the small dish was set up in the manner described in the experiment just referred to. The dish was nearly filled with a 16-per-cent. solution of HCl in distilled water. Three small fragments of zinc were thrown into it. A disk of sheet-zinc with a circle one inch in diameter, cut from its centre, was placed as a cover on the beaker. Over the aperture in the centre were placed, one above the other, 4 flat pieces of perforated zinc, the perforations being $\frac{1}{16}$ of an inch in diameter. The hydrogen had to fight its way through this barrier, and yet it carried with it the greater part of its charge, as the following notes of the experiment prove. The high-resistance Daniell gave a deflexion of 72 divisions either way.

| | Time. | Reading. |
|---|---|---|
| | h m | |
| Zinc dropped into acid. Cover placed on beaker. 4 flat zincs placed over aperture ..... | 3 23 | 365 |
| | 3 25 | 364 |
| | 3 27 | 363 |
| | 3 28 | 358 |
| | 3 29 | 343 |
| Spot comes to rest and returns ..... | 3 30 | 333 |
| | 3 31 | 333 |
| | 3 32 | 343 |
| | 3 33 | 353 |
| | 3 34 | 363 |
| | 3 35 | 373 |
| | 3 36 | 383 |
| | 3 37 | 383 |
| | 3 39 | 413 |
| Effervescence ceasing ..... | 3 42 | 413 |
| Quadrants short-circuited ..... ..... | 3 43 | 368 |

On examining the perforated zincs used in this experiment, each was found to have either spray or condensed vapour deposited on it, but the quantity on the lowest one was greater than that on any of the others. I was not, therefore, clear as to what part the spray played in the matter, and I set myself to consider what experiments I could make to clear up the point. Eventually I decided to make the following two, which I submit as decisive:—

(*a*) Every one has noticed that when hydrogen escapes from a generator containing acid and zinc, particles of the former are projected with considerable force from the vessel. I easily succeeded in catching these particles, or some part of them, on the metallic part of a proof-plane. I then touched the electrode of the insulated quads with the proof-plane, and found that the charge produced a deflexion to the left, indicating that the spray was of the same sign as the generator, and consequently opposite in sign to the charge carried by the gas. It also appears from this experiment that electrical repulsion among the particles themselves constitutes part of the force which causes their flight through the air.

(*b*) The bottom of a metallic goblet was perforated with holes about $\frac{1}{8}$ inch in diameter. It was then attached, mouth downwards, to the electrode of the insulated quadrants. A hydrogen-generator containing zinc and HCl was placed under it in such a position that the evolved gas passed right through the goblet. Almost instantly the spot moved rapidly to the right, which I had expected. The generator was now withdrawn. The spot slowly returned to within 5 divisions of zero.

Now if the electrification were due to spray, the goblet would retain its charge (the insulation was good); but being due to the hydrogen, which gradually passed through the perforations into the air, it very rapidly lost it.

In the course of these experiments I had often cast about for means of measuring the difference of potential arising from the contact of zinc and hydrochloric acid, and on consideration it appeared to me that this experiment presented a possible method. Particles of matter charged with electricity, and impinging on an insulated conductor, to which they give up part or the whole of their charges, could not raise the conductor

to a higher potential than they had attained ; but they, in the course of time, ought to bring it up to that level. My notion was to allow the charged hydrogen to flow through the goblet, fixed as described, long enough to ensure its reaching the potential of the gas ; then to remove the generator, and allow the gas to pass away through the perforations. The permanent deflexion then obtained ought, I considered, to be the measure of the quantity in question. I carried out with all the care possible several experiments on these lines ; but on account of the tenacity with which the gas holds its charge, I failed to get satisfactory determinations.

At this stage of my inquiry, I felt that I had got a few definite facts, that I had cleared up, at all events to my own satisfaction, many points which were at first doubtful, and that the theory of contact which I proposed was consistent with all the observations I had made. I proceeded to devise new experiments with the view of testing the truth, and determining the scope, of this theory.

Hydrogen passing through HCl and $H_2SO_4$ takes a positive charge ; passing through the corresponding salts of zinc it takes a negative charge. Then at any moment it ought to be possible to reverse the electrification by introducing into the vessel in which the reaction is going on acid or salt, as the case may be. The old experiment was made. Hydrogen was escaping from a 16-per-cent. solution of HCl, and the spot had travelled 100 divisions when a strong solution of zinc chloride was added. The spot went quickly back and up on the other side of the scale, showing that reversal had taken place. The addition of HCl produced a second reversal.

I had found hydrogen positive to two acids, and a question as to whether this was general often floated before me. I had no means of testing with nitric acid, because its action on metals does not give rise to hydrogen—at all events not in the final stage. I therefore directed attention to the other side of the question. Hydrogen was proved to be negative to chloride and sulphate of zinc. Was it possible that it was negative to other salts, or to salts in general ?

I again made the old experiment with $Zn + HCl$, and when a deflexion of 50 divisions was obtained a strong solution of

ferric chloride was added, with the effect of reversing the sign of the electrification. I proceeded to try other salts, such as NaCl, AmCl, $FeSO_4$, $MgSO_4$, $CaCl_2$, and found that these also produced reversal. I found, however, a few salts which did not do so, notably $Co(NO_3)_2$.

A wide principle thus appeared to be foreshadowed, viz., that hydrogen is positive to acids but negative to salts; but the number of cases examined does not warrant one in laying it down absolutely. Moreover, I have found that the hydrogen passing from acetic acid, whether by the use of sodium or iron filings, always comes off with a negative charge. I strongly suspect, however, that the reversal of sign in these cases takes place so rapidly that it escapes observation. I have had several instances of the spot moving a small distance to the left, suddenly turning, and moving far up on the opposite side of the scale. Occurrences of this kind leave no doubt on my mind that the first electrification (that due to the gas passing through the acid) is often small, owing, I think, to the rapidity with which the salt produced in the reaction diffuses.

Is hydrogen among gases unique in becoming charged when it passes through acids? was the question that next presented itself. I considered what reactions were likely to give any information with regard to the matter, and made numbers of experiments in the manner already fully described. I found that as a rule electrification results from any reaction giving rise to an escape of any substance into the air. In many cases the electrification is very trifling, and the electrometer must be in a sensitive state in order to show it. Of all the reacting combinations which I have tried, $HCl + Zn$ give by far the greatest difference of potential between generator and expelled gas. On the other hand, from $H_2SO_4 + NaCl$ I failed to get any trace of electrification. I give in the following Table *only* those reactions which by frequent repetition I have found to give constant results. I also give the estimated difference of potential, but shall postpone to a later stage a description of the method of making the measurement.

| Reacting substances. | Escaping gas. | Gas passing | | Quantity D. P. in volts. |
|---|---|---|---|---|
| | | Through acid. | Through salt solution. | |
| 1. $HCl+Zn$ ..... | H | + | − | 42 |
| 2. $HCl+CaCO_3$ ..... | $CO_2$ | + | − | |
| 3. $H_2SO_4+Na_2CO_3$ ..... | $CO_2$ | + | − | 9 |
| 4. $H_2SO_4+Na_2SO_3$ ..... | $SO_2$ | + | − | |
| 5. $HCl+Na_2SO_3$ ..... | $SO_2$ | + | − | |
| 6. $H_2SO_4+Zn$ (50% acid) | H | + | − | 16 |
| 7. $HCl+FeS$..... | $SH_2$ | + | − | |
| 8. $H_2SO_4+FeS$..... | $SH_2$ | + | − | |
| 9. $HCl$+Bleaching-powder | Cl | + | − | |
| 10. $H_2SO_4$+Bleach.-powder | Cl | + | Could not get this to reverse. | |
| 11. $HNO_3$+Bleach.-powder | Cl | Could not get the usual positive deflexion. | − | |
| 12. $HNO_3+CaCO_3$ ..... | $CO_2$ | Could not get positive deflexion. | − | |
| 13. $CH_3COHO$+Na ..... | H | Could not in either case get the normal positive deflexion. | − | |
| 14. $CH_3COHO$+Fe ..... | H | | − | |
| 15. $H_2SO_4+CaCO_3$ ..... | $CO_2$ | + | Could not get the reversal. | |
| 16. $H_2SO_4+NaCl$ ..... | HCl | Nil | Nil | |

It will be seen that there are nine instances in which the electrifications occur normally—that is to say, in which the charge is of one sign when the ejected gas passes through acid, but of the opposite sign when the corresponding salt gets into solution. I wish to direct special attention to the instances of abnormal behaviour, which I believe to be entirely due to the solubility of the salts produced in the reaction. When these get rapidly into solution and diffuse through the acid, the electrification due to the gas passing through acid cannot be obtained. There are two cases with $HNO_3$ and two with acetic acid where this happens, and we know that the salts derived from these acids are very soluble. On the other hand, there are two cases where $H_2SO_4$ takes part in the reaction, in neither of which could the electrification due to the passage of the gas through the solution of salt be obtained. In both instances sulphate of calcium is formed, and we know that this is rather insoluble. The ejected gas therefore never passed through a solution of salt. My contention here

derives great support from the fact that when $Na_2CO_3$ is used with $H_2SO_4$ to give $CO_2$, both deflexions are obtained. The only difference between the two reactions is that $Na_2SO_4$ is very soluble compared with $CaSO_4$.

Taking a broad view of these experiments, they appeared to me to indicate that, in general, gases were positive to acids, but negative to solutions of salts. I could not, however, throw off a feeling of dissatisfaction which arose from my not being able to suggest a trace of any *à priori* reason for such a thing. I fancied I saw some reason why hydrogen should be positive to acids and negative to salts; but that the generalization should be so wide as to extend to all gases, seemed to me most improbable. I felt disposed to question my theory of contact altogether, and resolved to make experiments of a different kind for the purpose of testing it.

If hydrogen be positive to hydrochloric acid, then, why not, I asked, prove it by a straightforward experiment such as passing a stream of the gas through the strong acid? Two insulated plates were set up near the electrometer and connected by a piece of copper wire. A beaker 2 inches in diameter and 5 inches high containing strong HCl was placed on one, and a hydrogen generator furnished with a narrow delivery-tube more than 12 inches long was set on the other. The delivery-tube was suitably fixed, and a brisk current of hydrogen passed through the strong hydrochloric acid. The hydrogen was found to come off with a positive charge, but on allowing it to get into the air direct from the delivery-tube it also came off charged in the same way. Here, then, I was balked. Of course the object of the long delivery-tube was to neutralize the gas before it touched the strong acid in the beaker. I have often remarked how firmly the hydrogen held its charge, but I was quite unprepared to find that it passed through more than 12 inches of wet glass tubing $\frac{1}{8}$ of an inch in diameter and escaped strongly electrified. I next passed the hydrogen through a wash-bottle, but it again came off charged. I passed it through all manner of bent tubing, made all possible shifts in fact to de-electrify the gas in order to fairly carry out my experiment, but without success. In sheer desperation I snatched up a litre-flask, filled it with water, and displaced the latter at the pneumatic

trough by hydrogen from Zn + HCl. I then placed the flask mouth upwards and open on the insulated plate which was connected to the quadrants. The spot gradually moved to the left, and came to rest at a distance of 180 divisions from zero.

This experiment yielded more food for thought. At first sight the deflexion appeared to be in the wrong direction, and I had to consider whether the hydrogen could, by any possible process, be neutralized.

I refilled the flask with hydrogen from zinc and hydrochloric acid and corked it before lifting its mouth from under the water, set it on the table, left it for $1\frac{3}{4}$ hours, then uncorked it and placed it on the insulated plate. A deflexion to the left of 100 divisions was gradually produced as the hydrogen left the flask. By repeated trials I found that it required from four to six hours to neutralize a flask or even a metallic vessel filled with hydrogen from zinc and hydrochloric acid.

But what of the deflexion in the wrong direction? On reflection, the explanation of the deflexion being to the left—that is to say, the insulated quadrants being negatively charged—very quickly appeared. The flask was held in the hand while being filled with hydrogen holding a positive charge. This acted inductively, repelling an equal quantity of positive to earth through my hand and body, and binding on the outside of the moist flask a charge of negative. When the flask was set on the insulated plate the hydrogen, owing to its lightness, gradually escaped into the air carrying its charge with it; and for every portion of the positively charged gas which left the flask a corresponding part of the negative charge bound on its wet outside was set free and spread over the quadrants, causing the deflexion. In fact the wet flask containing the charged hydrogen constituted a veritable Leyden jar.

I was anxious to verify this view. A hydrogen generator with a long neck and containing Zn + HCl was placed on the table. A large wide-mouthed wet flask was attached to an insulating handle, and, by means of this handle, was held mouth downwards in such position that the hydrogen from the long-necked generator filled it by displacing the air. It was then taken by means of the insulating handle *near* the insulated plate (which was connected to the insulated quadrants),

when the spot moved along the scale to the right, indicating that the quadrants were positively charged by the inductive action of the charged gas. The flask was next touched on the outside by the finger and again held *near* the insulated plate, but the spot did not move. This was quite in accordance with the Leyden-jar view, for the bound charge on the outside of the flask could have no effect on the insulated plate or the quadrants connected with it. The flask was now placed on the insulated plate, mouth upwards, and as the hydrogen escaped into the air the spot moved up the scale to the left, indicating that the bound negative charge on the outside of the flask was being liberated and charging the quadrants.

This afforded an instance of a kind of distribution of static electricity rather novel. I could only liken it to ground sulphur electrified by the grinding. Most instances of charged bodies are connected with surfaces, but here appeared a case where electricity pervaded an enclosed space. The only way in which I could figure it in my mind in connexion with the hydrogen was by furnishing each molecule of the gas with a charge with which it could not part until, in the ordinary movements of the molecules (according to the dynamical theory of gases), each came into actual contact with the moist inner surface of the flask containing the gas. This way of looking at it enables one to understand the slowness with which the electrified hydrogen becomes neutral; and as the time required to neutralize a vessel of gas of given shape and dimensions must be a function of the average velocity of its molecules at the existing pressure, suitable experiments may, possibly, lead to a direct determination of this quantity.

Musing over these experiments, the wet flask holding the charged hydrogen appeared, to me, not to differ materially from a soap-bubble blown with hydrogen from Zn + HCl. If there be anything in the notion, such a bubble should constitute a charged condenser with the binding charge completely enclosed. During the process of blowing it the repelled charge would pass to earth through the wet delivery-tube and generator. Figuring such a condenser floating through the air, I speculated as to how it would behave itself. As long as it remained in its integrity, no manifestation of its electrical condition could be given. Should the film, how-

ever, get fractured its nature would display itself. The gas containing the binding charge would instantly pass away, leaving the bound charge free on the water composing the shell, and it would pass to earth at the first opportunity.

Accounts have been given from time to time of curious bodies which make their way into dwelling-houses during periods of electrical disturbance in the air. They are described as gliding about, apparently examining nooks and corners, and often going up the chimney exploding (as it is called) on the way. Now if we consider a portion of electrified air enclosed by a film of some substance such as water, it would in most respects behave like a soap-bubble blown with hydrogen from zinc and hydrochloric acid. Being of nearly the same density as air, it would not rapidly ascend but move about, impelled by every slight draught. It would be a charged condenser, and the moment any rough or sharp prominence fractured the film, the bound charge would pass to earth, doing mischief in its track. Such an enclosure of electrified air might possibly be effected by an abnormal distribution of heat similar to that indicated by the formation of hail during thunderstorms. So close did the resemblance between my soap-bubbles and those "fire balls," as they are sometimes called, appear to me that I hastened to ascertain by experiment whether or not my speculations with regard to them comprised any truth.

Soap-bubbles were accordingly blown by means of the generator containing $Zn + HCl$. Only small ones could be obtained, and these shot away towards the ceiling so quickly that it was not easy to touch them with the metallic part of the proof plane. Some few, however, were caught and the proof plane was found to be very slightly negatively electrified. Some better plan had to be tried. The end of the delivery-tube was placed under the surface of the soap solution while gas was ecaping. A great mass of bubbles were produced on the surface, and some of them toppled over the side of the dish and fell towards the floor on account of the greater quantity of water in them. These were caught on the metallic part of the proof plane, and on testing the latter it was found to be strongly charged, the sign being negative,

which bore out the idea of the bubble being a charged condenser.

Another form of the experiment then occurred to me. The dish containing the soap solution was attached to an insulating handle and then set on the table. The end of the delivery-tube was once more dipped into the soap mixture, and a mass of bubbles was as before produced. The delivery-tube was then withdrawn, and the dish lifted from the table by an insulating handle. It was kept thus insulated until, in the course of a few minutes, the bubbles broke up, allowing the hydrogen to escape. The dish was then tested and found to have a negative charge. The soap-bubble blown as described was thus proved to be a charged condenser.

If by any process a mass of electrified air were enclosed by vesicles of water, or any other conducting material, a free charge would be developed on the outside which would cause the whole mass to be attracted or repelled according to the electrical state of proximate objects. In a recent number of 'Nature' I find an account of a thundercloud behaving in a manner at once explained by this hypothesis. The observer describes it as appearing to detach itself from a mass of cloud, gradually descend, and immediately after draw itself up again. The descent would be due partly to the attraction of the earth and to the repulsion of similarly electrified clouds above it. On touching the earth the free charge would escape, and the clouds, which at first repelled, would now attract, it, causing its ascent.

If such an enclosure of electrified air as I suggest were to occur at a high temperature in the upper regions of the atmosphere, its potential would gradually rise as it cooled and descended towards the earth; for the cooling of the mass of air, and the increase of pressure due to its less elevated position, would cooperate to lessen its volume, and, therefore, the surface of the enclosing film, while the quantity of electricity would remain the same.

Up to this stage I had used glass vessels in these experiments, but according to the view just set forth there could be no reason why a metallic vessel should not behave in precisely the same way. A tea-canister was accordingly filled with hydrogen by displacement of water from a generator containing zinc and hydrochloric acid. It was then placed on the

insulated plate, mouth upwards, and it was found that as the hydrogen escaped into the air the spot moved to the left, as had been expected ; and it was found on trial that everything that had been done with the glass flask could be done with one of metal. We have thus a condenser with only one conductor, and apparently without a dielectric ; and, from the ease with which it can be charged, and most of the properties of condensers demonstrated by means of it, one which may turn out useful for teaching-purposes.

A metallic flask filled with hydrogen by displacement of water from a generator containing Zn + HCl I found very instructive. It proved that hydrogen holds its charge with unexampled tenacity, for the vessel could be handled or left in communication with the earth for a considerable time without becoming neutral. It proved that spray or vapour of hydrochloric acid had nothing whatever to do with producing the electrification, for these were absorbed by the water over which the gas was collected. It also suggested a possible means of measuring the difference of potential due to the contact of hydrogen with hydrochloric acid. After a few trials, however, I gave it up, and decided to determine the quantity by Sir W. Thomson's "Water-dropper."

A metal funnel with a long stem was fixed to the insulated plate, which was as usual connected to insulated quadrants. The funnel was filled with water, and a series of drops fell from the nozzle of the stem. The drops broke away at a distance of 6 or 7 inches from the body of the funnel. An *uninsulated* dish 3 inches in diameter, containing Zn + HCl, was placed under the nozzle, so that the drops fell into it. As the hydrogen passed into the air, enveloping the nozzle and falling drops, the spot moved rapidly up the scale to right and off it. I withdrew some of the charge from the needle, and repeated the experiment. It again went off the scale. I withdrew a considerable quantity from the needle, and eventually reduced the sensibility of the instrument to such a degree that the deflexion never amounted to 300 divisions.

Fresh zinc and hydrochloric acid were now placed in the dish. The spot rapidly went up to 130 on the scale, from zero, and began to return. The "water-dropper" was then quickly disconnected from the quadrants, and the spot stood at 125. The dish was again supplied with fresh acid and

zinc and placed in position, and when I could see by the fumes that the nozzle was enveloped in the escaping gas I again connected the quadrants to the "water-dropper," when the spot moved up the scale higher. This was repeated as long as the spot could be forced to go higher. At 187 from zero it only oscillated right and left to the extent of 3 or 5 divisions, but could not be forced higher by the liberation of hydrogen near the nozzle from fresh acid and zinc. I took this number as measuring the potential above earth of the gas as it escaped from the acid.

The reason for changing the acid so frequently is to be found in the fact, which I had already proved, that when hydrogen passes through a solution of $ZnCl_2$ it comes off with a negative charge; and on this account, if the measurement be not made when the gas is passing through at the first stage of the reaction, the result cannot be correct. And, indeed, no matter what precautions are taken the result must be a little too small.

Several preliminary experiments of this kind were made, and when I was satisfied that the result was definite and constant I made very carefully the three following determinations. In each case the acid was changed *nine* times :—

| | Zero. | Deflexion. | Division. |
|---|---|---|---|
| (1) ..... | 362 | 552 | 190 |
| (2) ..... | 359 | 544 | 185 |
| (3) ..... | 358 | 545 | 187 |
| | | | 3)562 |
| | | | 187 |

I knew that I had reduced the sensibility of the electrometer very much, and when I proceeded to find the value of the scale-divisions in volts I found that the standard Daniell gave only a deflexion of from 3 to 6 divisions. Besides, this being very small I could not be certain of it to within a division, as the spot did not come precisely to zero. Of course, I could not attempt to base a calculation on so uncertain a quantity.

To get over this little trouble I set up five Grove cells in series, which gave a deflexion either way of 40 scale-divisions.

Therefore,

$$\frac{187 \times 5}{40} = \text{D. P. in Grove cells.}$$

$$\frac{1{\cdot}8 \times 18{\cdot}7 \times 5}{4} = \text{D. P. in volts.}$$

$$42{\cdot}08 = \text{D. P. in volts.}$$

The other numbers given were found in the same way. The potential of an electrified body depends on conditions, and the quantity I have determined may not be what I represent it. At all events, I have found approximately the potential above earth of a point in space immediately above the surface of the hydrochloric acid, through which hydrogen is passing. The distance between the surface of the acid and the drops where they broke away separately was 2 inches. If this distance were lessened another source of error would arise (or increase), for the particles of acid propelled by the hydrogen from the acid generator would strike the stem of the funnel and lessen the electrification, because, as has been proved, they are opposite in sign to the escaping gas.

But to return to my proposed straightforward experiment. I had intended to pass a current of neutral hydrogen through a column of strong hydrochloric acid, but found it impossible to neutralize the gas from a generator. However, I had now by trial become aware that a flask of hydrogen would become neutral after the lapse of some hours.

Three half Winchester quarts were filled with hydrogen by the displacement of water from a generator containing zinc and HCl, and were left during the night to lose their charges. At 8 o'clock the next morning one was uncorked and placed on the insulated plate. The hydrogen escaped, but the spot did not move. I was then pretty certain that the gas in the other two vessels was neutral.

A beaker, 7 inches high and 2 inches in diameter, was nearly filled with strong HCl, and a very slender delivery-tube, which had been attached to one of the vessels containing the hydrogen, was placed in it in such manner that any gas escaping from the vessel should pass right through a column of acid 6 inches high. An inverted metallic goblet was now attached to the insulated plate and quadrants, and placed in

such position that any hydrogen issuing from the beaker containing the acid should pass into it and be retained until it got into the air by diffusion. The hydrogen in the half Winchester quart was next forced through the acid by a stream of water. The spot did not move. No electrification was produced by the hydrogen bubbling through the acid. The experiment was repeated with the remaining half Winchester quart of hydrogen, but with the same result.

I had then to consider whether, in the face of this failure to electrify the neutral gas, I could reasonably stick to my theory of contact. I concluded that I could, and urge the following as sufficient grounds for my decision :—

I had proved beyond doubt that hydrogen holds a charge with amazing tenacity, and that it only gives it up when each molecule individually, it would appear, comes into contact with a conducting body. Such contacts were also proved to be most difficult to effect, and whatever difficulty exists in discharging the gas, by bringing it into contact with other substances, must also exist, and in a magnified form, when one tries to make contact between the gas and any substance for the purpose of charging. The difficulty of making real contact is not a new one. In fact, I hold that when the stream of hydrogen was forced through the pure acid, real contact was not made.

A very different state of things obtains when a piece of zinc is thrown into a quantity of acid. Here each molecule of hydrogen escapes from the chlorine into the acid separately, and very likely takes its charge while in the nascent condition. One cannot imitate the circumstances attending this condition of things by any possible arrangement of delivery-tubes, however small.

If it is proved that hydrogen or gases in general, in their nascent condition, take a charge when they come into contact with acids or solutions of salts, the fact, I should think, cannot fail to be of importance in the theory of the galvanic battery; and if it is proved that to make electrical contact between a gas and either metals or liquids is extremely difficult, what is known as "the air effect" in connexion with that theory appears to be negatived.

In conclusion, I wish to acknowledge the help in making

many of the experiments which I have received from Messrs. Horsnell and Leach, students at present passing through the college.

St. Mary's College, Hammersmith,
November 1889.

Prof. Rücker asked if the experiment with zinc and hydrochloric acid could be started in the second stage by having the acid partly saturated with salt.

Dr. C. V. Burton thought it probable that contact could be made between a gas and a liquid by shaking them up together in a bottle.

In reply Mr. Enright said the experiment could be started at any stage, and reversal effected as often as desired by adding either acid or a solution of salt to the generating vessel.

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## XLI. *The Effect of repeated Heating and Cooling on the Electrical Resistance of Iron.* *By* HERBERT TOMLINSON, *F.R.S.**

SOME of the physical properties of iron wire, even if it has been previously well annealed, can be considerably modified by repeatedly raising the metal to the temperature of 100° C., and suffering it to cool again. The internal friction, for instance, of a torsionally oscillating iron wire can be largely and permanently reduced by this process. Again, in a paper quite recently presented to the Royal Society, the author has brought forward an instance of an iron wire, which when made to go through magnetic cycles of very minute range, alternately at the temperatures of 100° C. and 17° C., was found to be permanently reduced, both in its molecular friction and its magnetic permeability, at each heating and cooling to such an extent that ultimately the former of these two physical properties became one quarter, and the latter less than one half of their respective original amounts. The large

* Read November 15, 1889.

The Author begs to acknowledge, with thanks, the assistance which he has received, in this and kindred investigations, from the "Elizabeth Thompson Science Fund."

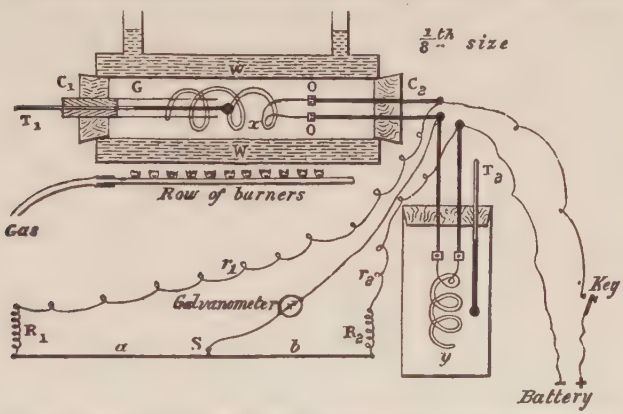
diminution of permeability and friction was also attended by a considerable lessening of the *temporary* effects of change of temperature on these properties. The object of the present investigation was to ascertain whether the electrical resistance and temperature-coefficients of iron would also be altered by the heating and cooling process. According to Matthiessen the electrical resistance of metals can be expressed by the formula

$$R_t = R_0 (1 + at + bt^2),$$

where $R_t$ and $R_0$ are the resistances at $t°$ and 0° C. respectively, and $a$ and $b$ are constants. For most pure metals the coefficient $a$ is not very far from ·00366, and the resistance varies, therefore, approximately as the absolute temperature; but with pure iron this coefficient is *much greater*. One of the questions which the inquiry was designed to answer was—Can the temperature-coefficient of iron be reduced by repeated heating and cooling to anything like ·00366? This question has been answered in the negative, but, at the same time, it appears that the electrical resistance itself suffers a small but decided change.

The iron wire examined formed part of a hank supplied by Messrs. Johnson and Nephew, and was specially prepared and annealed for the author by these makers; it was again annealed by the author himself in the following manner:— The piece of iron wire, together with several others, was placed in an iron tube about 130 centim. long; the tube and its contents were then heated, in one of Fletcher s new tube-furnaces, to 1000° C. This high temperature was preserved for several hours, and the wires were then allowed to cool slowly in the furnace. The above operations were repeated on three different days, so that eventually the wire was probably annealed as well as it could be by the ordinary method. In order to avoid any appreciable effect from the earth's magnetic force, the furnace was placed in a direction at right angles to the magnetic meridian. After the annealing the wire, which was about 120 centim. long and 1 millim. in diameter, was wrapped round with strips of paper, and wound double in a coil 5 centim. in diameter and 12 centim. in length. It was then placed in an air-chamber consisting of two co-axial

copper cylinders (see fig.) connected at their extremities, and enclosing between them an annular space filled with water. The whole arrangement is sufficiently shown in the figure.




In this figure O O are two clamps grooved so as to receive the ends of the iron wire $x$*, the clamps themselves being soldered to stout copper connecting-rods; a German-silver wire, $y$, is similarly connected, and placed in a glass vessel. $a\,b$ is a platinum-iridium wire of $\frac{1}{10}$ ohm resistance; $R_2$ is a resistance of 100 ohms, and $R_1$ a set of resistances from $\frac{1}{10}$ ohm to 200 ohms; the india-rubber-covered connecting-wires, $r_1$, $r_2$, have each a resistance of $\frac{1}{20}$ ohm at the temperature of 17° C.; and S is a sliding-piece which, by a suitable spring-and-catch arrangement, can be kept pressed on any part of $a\,b$. At the temperature of the room, the resistance of $y$ is nearly equal to that of $x$, and $R_1$ as well as $R_2$ is nearly 100 ohms; consequently, any slight changes which may occur during the experimenting in the temperature of $r_1$, $r_2$, and $a\,b$ do not sensibly affect the balance. The thermometers $T_1$ and $T_2$ register the temperatures of $x$ and $y$ respectively †; $T_1$ has

* If the grooves, and the ends of the wire which fit into them, be well cleaned, clamping serves quite as well, for the purpose of connexion, as soldering, and is more convenient.

† Only one thermometer was used for $T_1$ in this particular investigation, but the author generally employs, in work of this kind, three thermometers in turn. One of these thermometers is graduated from −5° C. to 30° C., the second from 30° C. to 65° C., and the third from 65° C. to 100° C.; all three thermometers are divided into tenth degrees, and have been carefully compared with the Kew standards.

its bulb in the centre of $x$, and is enclosed by the glass tube G; this tube is lined with india-rubber at the extremity outside the air-chamber, so that the thermometer can, if necessary for the purpose of reading, be pulled out to any required extent without causing any cooling; the glass tube and $T_1$ are both slightly slanted upwards to prevent the column of mercury from breaking when the temperature is falling.

For the purpose of preserving the temperature inside constant, the ends of the air-chamber are closed by corks, $C_1$, $C_2$, and the vacant spaces inside are stuffed with cotton-wool (not shown in the figure). The water in the annular space W is heated by a row of burners, made by piercing pin-holes at equal intervals in a copper tube, closed at one end, and connected at the other with the gas. By adjusting the supply of gas or by altering the distance of the row of burners from the air-chamber, any required temperature up to 100° C. could be maintained nearly, if not quite, constant for a considerable length of time. In 15 minutes the water could be raised to 100° C.; and then, by diminishing the supply of gas so that the water only just boiled, this temperature could be kept up for 16 hours without adding more water; when it was necessary to maintain the temperature at 100° C. for longer periods of time, the vessel was replenished with boiling water.

It will be seen from the figure that there is a "Wheatstone's Bridge" arrangement for determining the resistance-ratio, $x : y$. The temperature of $y$ varied by only a few degrees during the whole of the inquiry; and as both the actual resistance of the coil at 17° C. and its temperature-coefficient were known, the resistance of $y$ at any other temperature could be calculated.

It is usual in experiments with the "bridge" to close first the battery-circuit, and immediately afterwards that of the galvanometer; but the author prefers to keep the galvanometer-circuit always closed, and to observe the effect of closing the battery-circuit. It is true that in the latter case there is always a momentary throw of the needle due to self-induction in the wires, but this, with the arrangement shown above, is very slight; and with no more delay than that of two or three seconds, it can be easily ascertained whether the act of closing the battery-circuit causes *any alteration in the difference*

*of potential at the galvanometer-terminals**. If, on the contrary, the former of the two methods be employed, there arises more or less inaccuracy from the presence of thermo-electrical currents set up in one or more branches of the bridge by slight variations in the temperature of the air at different parts of the room. Besides, even if the air could be maintained at perfectly uniform temperature throughout, thermo-electrical currents are always produced by the act of pressing down the sliding-piece, S, on the wire $ab$, and by Peltier effects.

The act of bending the wire into the form of the coil produced, as might be expected, a slight permanent change in its resistance, which was thereby increased by $\frac{1}{4}$ per cent.; doubtless a portion, but only a small one, of the whole reduction of resistance, to be presently recorded, is to be attributed to the partial or complete removal of the effect of coiling.

When everything was ready, and the wire had been left undisturbed for several hours, its resistance and temperature were determined; the latter was then raised to 100° C., or very nearly to 100° C., and maintained thereat for at least 8 hours†; and during this period the resistance of the wire was tested several times. The wire was then permitted to cool down, and its resistance was again determined about 16 hours afterwards. The same operations were repeated again and again, until the metal showed that no sensible change of resistance was produced by the heating and cooling. The results are given in the following Table (p. 322).

It will be noticed that the specific resistance both at 17° C. and at 100° C. is diminished with each repetition of the heating and cooling process, until, finally, it becomes about $4\frac{1}{2}$ per cent. less than at first. Thus, though the permanent effect on the electrical resistance is very much less than that on the permeability for very minute magnetizing forces, it is quite sensible.

At the sixth heating the wire was kept at 100° C. for 26 hours and, moreover, the battery-current was applied first in

* There is always a difference of potential at the galvanometer-terminals arising from thermo-electrical effects; see what follows.

† The deviation from 100° C. never exceeded $\frac{3}{10}$° C., and could in all cases be accounted for by changes in the barometric pressure.

| Number of times heated to 100° C. | Specific resistance in C.G.S. units at 17° C. $R_{17}$. | Differences between consecutive values of $R_{17}$. | Specific resistance at 100° C. $R_{100}$. | $R_{100}-R_{17}$*. | $\frac{R_{100}-R_{17}}{R_{17}}$*. | Remarks. |
|---|---|---|---|---|---|---|
| 0 | 11162 | | | | | |
| 1 | 10942 | 220 | 16029 | 4952 | ·4527 | Kept at 100° C. for 8 hours; the battery-current always applied in the same direction. |
| 2 | 10807 | 135 | 15796 | 4922 | ·4526 | Ditto. |
| 3 | 10772 | 35 | 15789 | 4985 | ·4613 | Ditto. |
| 4 | 10757 | 15 | 15747 | 4999 | ·4633 | Ditto. |
| 5 | 10755 | 2 | ..... | 4996 | ·4638 | Ditto. |
| 6 | 10727 | 28 | 15724 | ..... | ..... | Kept at 100° C. for 26 hours; the battery-current applied first in one direction and then in the opposite. |
| 7 | 10711 | 16 | 15679 | 4983 | ·4629 | Kept at 100° C. for 8 hours; the battery-current applied first in one direction and then in the opposite. |
| 8 | 10694 | 17 | 15674 | 4965 | ·4636 | Ditto. |
| 9 | 10689 | 5 | ..... | ..... | ..... | Ditto. |
| 10 | ..... | ..... | 15654 | ..... | ..... | Ditto. |
| 11 | ..... | ..... | ..... | ..... | ..... | Ditto. |
| 12 | 10688 | ..... | ..... | ..... | ..... | Ditto. |

* For the mode of calculating the numbers in these columns, see what follows.

one direction and then in the opposite. These reversals of the current served to increase the rate of diminution of the resistance.

The maintaining the temperature at 100° C. for 26 hours did not diminish the resistance as much as the next two heatings and coolings taken together; evidently, therefore, the cooling exerts an influence as well as the heating. It is not, in fact, of much use prolonging each period of heating beyond 8 hours, whilst, on the contrary, a less time will hardly suffice, heating and cooling in rapid alternation being comparatively ineffectual.

Though the specific resistance of the annealed iron is permanently diminished by the heating and cooling process, this is not so with the *temporary* change of resistance arising from change of temperature; the sixth column of the Table shows that the temporary increase of resistance produced by raising the temperature from 17° C. to 100° C. is not affected by the heating and cooling process, whilst the temporary increase of resistance *per unit* becomes greater in proportion as the specific resistance itself becomes less.

The values of $R_{100}-R_{17}$ and $\frac{R_{100}-R_{17}}{R_{17}}$ were calculated so as to avoid, as much as possible, error arising from the *permanent* changes consequent on the heating and cooling. Let $C_1$, $C_2$, $C_3$, &c., represent the resistances of the cold wire after the first, second, third, &c., heatings, and $H_1$, $H_2$, $H_3$, &c., the corresponding resistances of the hot wire, then the numbers in the sixth column were obtained from $\frac{H_1+H_2}{2}-C_1$, $H_2-\frac{C_1+C_2}{2}$, $\frac{H_2+H_3}{2}-C_3$, $H_3-\frac{C_3+C_4}{2}$, &c., and those in the last column by dividing these by $C_1$, $\frac{C_1+C_2}{2}$, $C_3$, $\frac{C_3+C_4}{2}$, &c., respectively. Of course, the temperature of the room was not always 17° C., but the resistance of $x$ at 17° C. could be calculated from its actual resistance at the temperature at the time by means of a formula ultimately obtained for the resistance of the wire at any temperature *. This formula

* Similarly for the higher temperature of 100° C.

was calculated from the results of a number of very careful observations at 17° C., 60° C., and 100° C., and after the heating and cooling process had ceased to affect the resistance. The formula thus obtained was :—

$$R_t = R_0 (1 + \cdot 005131\, t + \cdot 00000815\, t^2);$$

whilst the formula deducible from Matthiessen's results for *pure* iron annealed in hydrogen is

$$R_t = R_0 (1 + \cdot 005425\, t + \cdot 0000083\, t^2).$$

The specific resistance at 0° C. ($R_{0 \cdot T}$) of the author's iron was 9808 electromagnetic units, whilst that of Matthiessen's pure iron ($R_{0 \cdot M}$) is given on the authority of the late Prof. Jenkin as 9718*. It seems not improbable that this last value is from 4 to 5 per cent. too high ; for it follows from Matthiessen's researches that the resistances at any temperature of a pure metal and its alloy should be in the inverse ratio of the rates of increase of resistance at that temperature, so that

$$\frac{R_{0 \cdot M}}{R_{0 \cdot T}} \text{ should equal } \frac{\cdot 005131}{\cdot 005425},$$

which, if the author's result be assumed to be correct, would make $R_{0 \cdot M}$ equal to 9277.

Unfortunately, Matthiessen did not determine the *absolute* resistance of iron and many of the other pure metals examined by him, and it appears from Prof. Jenkin's own statement† that the calculated results for these metals cannot be depended on for any great degree of accuracy. The author, therefore, ventures to express the hope that the B. A. Electrical Standards Committee may be induced to determine the absolute resistances and the temperature-coefficients of those of the pure metals which are in ordinary use.

* The number actually given by Prof. Jenkin has been multiplied by ·9889 (the value of the B.A. unit in terms of the legal ohm).

† See note on p. 250 of Prof. Jenkin's book on 'Electricity and Magnetism.'

Dr. Walmsley asked for what value of the magnetizing force the permeability of the iron mentioned in the beginning of the paper was determined; to which Mr. Tomlinson replied that they were much smaller than the earth's horizontal component.

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## XLII. *The Electrification of a Steam-jet.*

*By* Shelford Bidwell, *M.A., F.R.S.**

The boiler used in these experiments consists of a small tin bottle capable of holding about fifteen fluid ounces, which is supported upon a tripod above a Bunsen burner. Its neck is fitted with a cork, through which passes a glass tube $\frac{5}{16}$ in. in diameter, terminating in a nozzle with an opening of about $\frac{1}{16}$ in. At a point four inches above the cork, the tube is bent to an angle of 100 or 110 degrees, and the nozzle may be formed at a distance of five or six inches from the bend. In this case its direction will, of course, be nearly horizontal. When it is desired to have a vertical nozzle, the tube is again bent in an upright direction at a distance of not less than five inches from the first angle, the nozzle terminating two or three inches above the second bend. The nozzle is made by simply drawing out the tube to a point in a flame, and cutting off its end at the proper place.

I have given these dimensions in detail, not, of course, because they are absolutely the best possible, but in order that anyone who wishes to repeat the experiment may be enabled to obtain good results without trouble. The object aimed at is to keep the tube as free as possible from water, whether arising from ebullition or from condensation, so that the jet of steam may be regular and uniform; at the same time, it is essential that the end of the nozzle from which the steam issues should not be directly above the gas-burner, or the experiment cannot succeed.

The tin bottle is charged with four ounces of water, and when it boils the burner is adjusted until the steam-jet is as

* Read December 6, 1889.

vigorous as is possible consistently with steadiness ; if the ebullition is too violent, the water thrown up into the tube will produce jerks, masking the effect to be looked for.

The jet is most conveniently observed by means of its shadow projected upon a white screen. For this purpose a lime-light is desirable, but any good source of light may be employed. The shadow of the jet will be seen to be of feeble intensity and of a neutral tint ; the jet is, in fact, nearly transparent, and does not appear to exercise any selective absorption upon the light. If now a sharp point, or, better, a small bundle of points, in connexion with one of the terminals of an influence-machine (such as a Voss), is brought near the base of the jet, the machine being worked slowly, a startling change instantly comes over the shadow. It becomes dark and dense, at the same time assuming a marked orange-brown tint. By removing the point, or simply connecting it to earth, the shadow can be immediately caused to resume its original appearance, again becoming almost invisible. This operation may be repeated as often as desired, one of the most remarkable things about it being the extreme rapidity with which the changes are produced.

The point need not necessarily be directed to the origin of the jet ; it is nearly as effective when placed in the steam at a distance of a foot or more from the nozzle ; and in such a case the *whole* of the steam-jet is equally acted upon from its origin onwards, even when the direction of the point is the same as that of the jet. A ball may be used instead of a point, but it operates only when actually within the jet, whereas a point may be outside it. The effect may also be produced by directing the jet upon an electrified metal disk, supported at a considerable distance from the nozzle.

I have examined the absorption-spectrum of the steam-jet. When the jet is not electrified, its action upon the spectrum is small, the intensity of the whole being slightly diminished in an apparently equal degree throughout. Possibly the violet is dimmed in a somewhat greater proportion than the other colours. Electrification of the jet causes the violet to disappear completely, while the luminosity of the blue and the more refrangible part of the green is materially decreased. The orange and red are, I believe, quite unaffected.

From these facts it may be concluded that electrification causes an increase in the size of the water particles contained in the steam-jet. In the unelectrified condition the majority of these particles are small in relation to a wave-length of light; under the influence of electrification they become larger, and attain a diameter of something like a fifty-thousandth part of an inch.

The idea naturally suggests itself that the phenomenon may be of the same nature as that observed by Lord Rayleigh in the case of water-jets*. A stream of water issuing in a nearly vertical jet from a small orifice is found to break up into separate drops at a certain distance above the orifice. Under ordinary conditions these drops collide with one another, and, again rebounding, become scattered over a considerable space. But when subjected to the influence of an electrified body, as a rubbed stick of sealing-wax, brought near the point of resolution, the colliding drops no longer rebound but coalesce, and the entire stream of water, both ascending and descending, appears to become coherent. Now it seems to me certain that the innumerable minute particles of water generated in the steam-jet, each consisting perhaps of only a few molecules, must necessarily come into frequent collision with one another; for we cannot suppose that they all travel with equal velocities and in exactly the same direction; and there is no reason why they should not behave just in the same manner as the larger drops of the water-jet, rebounding when they are not electrified, coalescing into larger drops when they are. It is true that the degree of electrification required to produce the phenomenon in the case of the steam-jet is apparently much greater than in the other, a rubbed stick of sealing-wax being altogether inoperative. Perhaps this is a consequence of the different sizes of the drops in the two cases. That the actual electrification of the particles in the steam-jet is really very small indeed, is proved by the fact that if two electrified steam clouds are generated in close proximity to each other, they exhibit little, if any, evidence of mutual repulsion when they are similarly electrified, or of attraction when their electrifications are of the opposite kind.

* Proc. Roy. Soc. 1879.

Lord Rayleigh shows cause for believing that if the electrifications of the drops in the water-jet were strictly equal, the phenomenon in question would not occur; and the reasons why they are not, in fact, equal would just as well apply to the case of the steam-jet. How unequal charges of electricity of the same name are operative in bringing about coalescence Lord Rayleigh does not explain, nor am I prepared to hazard a conjecture on the point.

Lord Rayleigh concludes his paper by referring to the importance of the investigation from a meteorological point of view. I may do the same. It seems certain that the steam-jet experiments go far towards explaining the cause of the intense darkness which is characteristic of thunder-clouds, as well as of the lurid yellow light by which that darkness is frequently tempered.

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I had made the above described experiments and drawn the above stated conclusions concerning them, and had just requested the Secretary of the Physical Society to accept the present communication, when Prof. Silvanus Thompson, whose knowledge of scientific history is proverbially encyclopædic, was good enough to bring to my notice the fact that experiments upon the electrification of a steam-jet had been recently made in Germany by the late Robert Helmholtz. An account of these experiments, which are of the greatest interest, is given in Wiedemann's *Annalen*, vol. xxxii. p. 1. The author appears never to have examined his jets by transmitted light, and makes no mention of the marvellous increase of opacity under electrification, to which I have called attention. His observations were all made against a *dark* background, the illuminating beam of light coming obliquely from the front, but shaded from the eyes. When the jet is electrified, he says, it is at once seen more clearly and sharply against the background; it also assumes diffraction colours, like those seen in strata of fog. Very strong electrification produces a deep blue colour, indicating the formation of very small mist drops. On slowly diminishing the electrification the blue tint at first becomes gradually paler, which points to the formation of larger drops; and it is then succeeded by tints of purple, red, yellow, green, and finally, when the discharge is very feeble, by pale blue tones again. Under

certain circumstances all these several tints may be seen at once in different portions of the jet.

I, too, had observed these diffraction colours, which were sometimes very beautiful; but having convinced myself that they undoubtedly occurred at times when no electrical influence (that I knew of) was operating, I did not follow up the observation.

Helmholtz found that these condensation phenomena could be just as well produced by some other causes as by electrification, and especially by the agency of flame. All the exciting causes in question involve some continuous chemical action inside the steam-jet. He conjectures, therefore, that the sudden condensation may be due to molecular tremors or shocks, which upset the unstable equilibrium of the supersaturated vapour, just as a small disturbance will sometimes cause the sudden crystallization of a supersaturated saline solution; and after showing that chemical reactions may occur freely even outside the visible portion of a flame, he states his opinion that similar dissociations and recombinations take place among the molecules of the air affected by an electric discharge, as evidenced, for instance, by the formation of ozone.

A very striking illustration of the effect of combustion is afforded by holding beneath the jet a piece of burning touch-paper, made by soaking blotting-paper in a solution of nitrate of lead. The jet at once becomes quite as opaque as if electrical influence were employed, and the same hissing noise is also heard. The burning touch-paper suggested itself as more convenient than the actual flames used by Helmholtz for the purpose; for these cannot be brought underneath the jet without causing its immediate dissipation; and it is therefore necessary to hold them on one side, and direct their heated gases upon the jet by blowing or fanning.

After reading Helmholtz's paper it naturally occurred to me to try the effect of combustion upon the water-jet. In this case the objection to the use of an actual flame does not, of course, apply. I therefore introduced the flame of a Bunsen burner into the jet, and found that, if the air-holes were stopped up, and the flame thus rendered luminous, a decided effect was produced upon the jet. Often, indeed, it became just as completely coherent throughout its length as if it were electrified, though I have not yet succeeded in

obtaining this result with perfect certainty; but in every case when the burner was held a little below the point of resolution, a considerable diminution of the scattering was observed. If the air-holes were opened and the flame made non-luminous, it failed to act in any way whatever upon the jet. It is to be remarked that Helmholtz found certain non-luminous flames (of which, however, a gas-flame was not one) to be devoid of influence upon the steam-jet.

Can the effect here also be due to electrification? It can hardly be attributable to heating, because the flame of a Bunsen burner is certainly hotter when it is non-luminous than when it is luminous. On the other hand, it is known from many experiments that flame is electrified. If, for example, we place a luminous flame between the positive and negative ball-terminals of a Voss machine in action (the terminals being too far apart for sparks to pass), we find that the flame, or at least the upper part of it, is repelled by the positive and attracted by the negative ball. This seems to denote positive electrification of the flame.

In conclusion, it should be mentioned that Helmholtz suggests another hypothesis as an alternative to that of molecular shock, though he does not appear to attach much importance to it. It is that the electrical discharge, the flame or other exciting agent, whatever it may be, acts by introducing into the steam-jet minute particles of solid matter which serve as nuclei upon which the water-vapour may condense, as in Aitken's experiments on the formation of fog.

It is possible that several different causes may be competent to produce the condensation phenomena.

Prof. Rücker said Mr. Bidwell had no doubt considered the question, but he should like to ask him whether he thought the behaviour of the jet when the burning paper was held under it might not be due to a lowering of its surface-tension. Though the length at which a liquid cylinder becomes unstable is independent of the tension, the rate at which the transformation into drops takes place depends on it, and thus the distance from the orifice at which discontinuity is established would vary with the state of the surface.

Mr. Richardson inquired whether a red-hot iron had any effect.

Dr. Fison said he had made experiments on the electrification of flame, and found that potentials varying from +2 volts to $-1\frac{1}{2}$ volt could be obtained in the region within and surrounding a Bunsen-flame.

Prof. S. P. Thompson commented on the contrast between Mr. Bidwell's experiments and those of Dr Lodge on the dissipation of fogs by electricity, and also asked whether the colour of the jet depended on the length of spark produced by the machine.

Prof. Forbes thought a crucial test between the two hypotheses of Helmholtz could be obtained by trying the experiment in a germless globe.

The President said he had recently noticed that gas-flames were electrified.

Mr. Bidwell, in reply, said that since writing the paper it had occurred to him that the effect of flame upon the water-jet might possibly be due rather to the introduction of dirt into the stream than to electrification, Lord Rayleigh having observed that scattering did not occur if a little soap or milk were added to the water. He thought that the colour assumed by the electrified steam-jet appeared generally to be independent of the sparking-distance. He had not tried whether a red-hot iron produced any effect.

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## XLIII. *On the Behaviour of Steel under Mechanical Stress.* By C. A. Carus-Wilson, *B.A., A.M.I.C.E., Demonstrator in the Mechanical Laboratory at the Royal Indian Engineering College, Coopers Hill**.

[Plates IX.–XI.]

The effect of uniform longitudinal stress on a steel bar is threefold :—

(i.) The molecules are strained.

(ii.) The elements are strained.

(iii.) In virtue of the straining of the elements "flow" is produced.

The strain usually observed is the elongation due to flow, which may be recoverable or irrecoverable. The strains of an element can be shown to be a uniform dilatation combined

* Read December 6, 1889.

with a uniform shear about an axis parallel to that of the bar; hence the elongation due to flow consists of a sliding combined with an increase of volume.

The state of strain of an element may be conveniently described by defining the shape, size, and orientation of the strain quadric, which is a sphere of radius $3\sqrt{\frac{k}{p}}$ combined with an hyperboloid of two sheets whose principal semi-diameter is $\sqrt{\frac{3n}{p}}$ and axis parallel to that of the bar; where $p$ is the intensity of longitudinal stress, $n$ the rigidity, and $k$ the bulk modulus.

Up to a certain stress the elastic properties of the steel are such that the strain produced is recovered when the load is removed, but at that stress the elastic resistance is overcome, and the molecules slide over one another, the strain being permanent.

This sliding beyond the limit of elastic resistance does not continue. The elastic resistance is raised by the sliding, and consequently the sliding is limited.

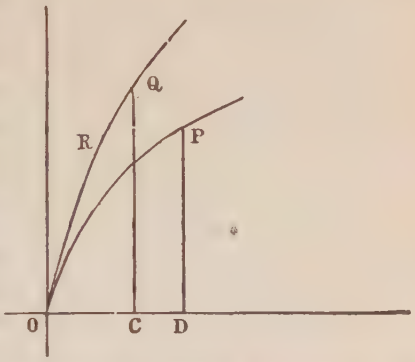
A stress-strain curve can be drawn which shows the increase of the limit of elastic resistance $\rho$ with sliding; the rate of increase of the former at any point may be measured by observing the angle which the tangent to the curve at that point makes with the axis of strain; I will call this angle $\phi$.

The initial value of $\rho$ is often taken as an indication of the "hardness" of the steel, and when $\rho$ is raised by permanent strain the steel is said to be "hardened" thereby. This, however, conflicts with a measure of hardness usually employed, namely the amount of permanent strain caused by performing a given amount of work on a bar.

Thus if a hard steel edge attached to a weight is allowed to fall on the surface of a steel bar, the depth of the indentation is taken as a measure of the softness of the metal.

If we draw the stress-strain curve O P for the steel under examination, the work done in producing a permanent strain O D is the area O P D. If O Q represent the stress-strain curve of a harder bar, the same amount of work, O Q C, will clearly produce less permanent strain, O C. The hardness then is evidently determined by the form of the curve; but

this depends upon the rate of increase of $\rho$ with permanent strain, *i. e.* upon the value of $\phi$. Hence $\tan\phi$ is the true measure of the hardness; but $\tan\phi$ is not constant, it diminishes: therefore the initial value of $\tan\phi$ must be taken as the measure of hardness. It will be seen that $\rho$ cannot be taken as a measure of the hardness, for $\rho$ is the same at R and P for the two bars, but the former is obviously the harder*.




We can say, then, that permanent strain raises the limit of elastic resistance, but diminishes the hardness—defined as the rate of increase of $\rho$ with permanent strain.

I imagine it is because the harder steel has the greater value of initial $\rho$ that $\rho$ has been taken as a measure of the hardness.

If a bar of soft steel be taken and cut in four pieces; No. II. "hardened" in oil; No. III. in water [alkaline]; No. IV. in water [acid]; if each piece is now tested we shall obtain stress-strain curves as in fig. 1, Plate IX. A curve can be drawn through the points O A B C D E F, which I will call the "yield-line"; this will be the locus of all points such as A and F for pieces of the same bar "hardened" to different degrees. The points A, B, C are called the "yield-points."

As the piece is harder the yield-point—or initial limit of elastic resistance—is higher, and the yield A F is less†.

When the yield begins it continues until $\rho$ is raised by a given amount $\lambda$. If we could show that $\lambda$ was the same for each piece, then it would follow that the yields as A F, B E, C D are direct measures of the hardness of the piece.

If there is any inequality or want of homogeneity in the bar due to unequal stresses in the manufacture, there may be

* If $\tan\phi=0$, the bar at that point is perfectly plastic.

† Fig. 2, Plate IX. is a facsimile of an autographic diagram thus obtained: the steel bar was cut in three pieces; A was soft, B hardened in oil, and C in acid.

one plane or planes along which the limit of elastic resistance is less than along any other.

Hence when this resistance is overcome sliding will take place throughout the bar parallel to that plane or planes until the limit of resistance along that plane has been raised, by the sliding, to that of the rest of the bar, when the sliding will henceforth be uniform.

In a bar cut into pieces the required increase is the same in each piece, only in the harder bar less permanent strain is required than in the softer. Hence $\lambda$ is the same in each piece and the yield is a measure of the hardness.

Steel bars and plates can be shown in which the permanent strain at the yield-point has clearly taken place as a sliding parallel to one plane only.

It would seem that there was an apparent discontinuity in the form of the stress-strain curve at the yield-point.

The question arises whether the curve may not actually be continued through a double inflexion, and be one with the rest of the curve as shown by the dotted lines, fig. 1, Plate IX.

Let us imagine a solid model made so as to represent at any point of its surface a particular condition of the bar with respect to stress, strain, and hardness. Let the curves I., II., III., IV. (fig. 1, Plate IX.) be placed parallel to one another at distances from the plane X O Y proportional to the hardness which each curve represents, with their origins in the axis O Z (perpendicular to X O Y), and let the surface of the model be made to pass evenly through all these curves and other similar curves which would be obtained at higher and lower degrees of hardness.

We see that from the curve which just passes outside the yield-line there is a part of the solid figure entirely wanting. It would seem a much more natural view to suppose that in some sense the successive curves are theoretically continuous, as shown by the dotted line above.

Such a supposition involves a state of affairs in which the limit of elastic resistance decreases as the permanent strain increases.

This would be the case if the sliding at the yield-point instead of taking place simultaneously over the whole bar parallel to one plane only took place as a strain wave passing

up or down the bar with a definite velocity without any further increase of load.

This is what actually takes place. Sliding is started at one end and takes place along a definite plane, generally at 45° to the axis; this disturbs the equilibrium of the molecules in the parallel plane next to it, and sliding is induced in this plane, so that a wave of strain passes the whole way up the bar; or sometimes starting from both ends two waves meet in the centre.

The velocity of the wave varies greatly with the quality of the steel; sometimes the wave appears to be instantaneous, sometimes so slow that it may take 30 seconds to pass up a 10-inch bar, in which case the pencil drawing the stress-strain curve is seen to follow the wave; in the former case the pencil drops as if the bar had broken.

When the wave starts from one end a plane in the centre experiences no permanent sliding until the wave has reached the plane next to it, so that while originally the resistance to sliding was greater than the stress, now it is less; in other words, permanent strain (in an adjacent plane) diminishes the resistance to permanent strain.

The most reliable stress-strain curves are those drawn by Prof. Kennedy's apparatus, and these show a rapid and irregular inflexion at the yield-point (see fig. 3, Plate IX.). In these diagrams the record of stress is unaffected by the inertia due to the load.

These stress-strain curves indicate the condition of strain in a steel bar as, by gradually increased stress, the steel is converted from an elastic solid to a viscous fluid. It is interesting to compare such curves for steel of different hardness with the stress-strain curves of a gas at different temperatures (see fig. 4, Plate IX.).

We have the effect of increased $\left\{\begin{matrix}\text{hardness}\\\text{temperature}\end{matrix}\right\}$ doing away with the discontinuity at the $\left\{\begin{matrix}\text{yield}\\\text{boiling}\end{matrix}\right\}$ line. Also the strong probability that in both cases the apparent discontinuity is really a double inflexion due to a change taking place piecemeal throughout the substance, and inconceivable if the substance be supposed homogeneous (*cf.* Prof. J. Thomson, Proc. Roy. Soc. 1871, no. 130).

[The stress-strain curves shown in the diagram are from Dr. Andrews's paper (Phil. Trans. vol. clix. 1869, p. 575).]

Thus far the strains considered have been those due to relative displacements of the molecules, but it is impossible to conceive that this can take place without the molecules themselves being strained, *i. e.* without a displacement of the atoms.

Such a displacement of atoms, if permanent, would alter the chemical and physical condition of the iron. Hence we must look to the straining of the atoms to account for the change that takes place when a bar is permanently strained, *i. e.* to account for the increase in the value of $\rho$ with permanent strain.

Osmond has proved almost beyond a doubt that the so-called "hardness" of steel is due essentially to the existence of an allotropic modification of iron; that the molecules of iron may be either ($\alpha$) soft, or ($\beta$) hard. (*Cf.* Osmond's *Etudes Métallurgiques*, Paris, Dunod, 1888.)

Hence the change induced in steel by permanent strain must be due to a permanent straining of the atoms in the molecule.

We should then expect to find evidence of a straining of an entirely different order and nature to that due to a molecular disturbance. Such evidence is forthcoming.

It has long been known that if a steel bar lying in a magnetic field of limited intensity be subjected to tension in the direction of the magnetizing force, the magnetization of the bar will be increased.

I have made a series of experiments on this subject, and find that the intensity of magnetization increases regularly with the load up to the yield-point.

The following experiments were made:—

The bar to be tested was turned in the lathe, and a screw cut on each end; it was placed vertically in the testing-machine; to each end was screwed a nut, the top one (A) of gun-metal, the lower one (B) of steel (see fig. 1, Plate X.). The former was of gun-metal so as to remove the free upper extremity of the bar as far as possible from the neighbourhood of large masses of magnetic material. These nuts rest on steel collars, C C, which have conical surfaces to fit into conical holes in the main shackles, D D, of the testing-machine. The bearing of the nuts on the collars is spherical, so as to

allow of a free movement of the specimen, and to ensure a direct pull. A short distance above the upper end of the bar a small magnet, E, is hung by a silk fibre, the suspension of which is rigidly attached to the upper shackle, so that any small motion of the latter involves the same motion of the needle; a silvered mirror is attached to the needle, which reflects a beam of light from a lamp, F, onto a horizontal scale, G; H is a controlling-magnet.

A small displacement is given to the magnet (i.) when there is no load on the bar, and the time of 20 complete oscillations observed; (ii.) the same with a small load on; (iii.) the load is then removed, and the time of 20 oscillations again observed. The results are recorded in the accompanying Table.

*Experiment I.*—Bar of soft steel, never loaded before: cross sectional area 0·306 square inch, 19·5 inches long; elongations measured on 10″ by a vernier and microscope reading to thousandths of an inch.

An automatic stress-strain diagram was taken (see curve A, Plate X.). The time of 20 oscillations of the needle was first observed with the bar out—102·6 seconds. From this was deduced $x^2$, the square of the number of oscillations per minute, and this was deducted from $N^2$, the same when the bar was in place. The results are plotted on fig. 1, Plate XI., as two curves, the upper one, $A_1$, being the curve of temporarily-induced magnetism, with load on, and the lower one, $A_2$, that of permanent magnetism, with load off. The arrow shows the yield-point. The two curves cross one another twice, and coincide in a third point. The third curve, $A_3$, is the curve of extensions from the second column of the Table, 186 times full size. Curve $A_4$ is the curve of permanent set, same scale as $A_3$. This bar was broken. The last observation was after the fracture.

*Experiment II.*—Bar of soft steel never loaded before: cross-sectional area 0·308 square inch, 19 inches long; diagram measures elongations of 10″; square of number of oscillations per minute with bar out 121; ditto, bar in, no load on, 1849. The results are plotted as a curve in fig. 2, Plate XI. The arrow shows the yield-point. The observations at this point were taken after the set. The stress-strain diagram is shown at B, Plate X. This bar was broken.

*Experiment III.*—Wrought-iron bar never loaded before: cross-sectional area 0·203 square inch. The extensions on the diagram, C, Plate X., are on a length of six inches. The results are recorded in the Table, and plotted on fig. 5, Plate IX., the ordinates here representing simply the square of the number of oscillations per minute. The arrow shows the yield-point. The curves intersect twice. This bar was not broken.

The circles show the loads at which observations were made.

From the curves on Plates IX. and XI., it is evident that the magnetic induction is increased in a regular way by increased stress, and that the effect is largely permanent; a point is reached, before the yield-point, where the effect produced is wholly permanent. The two curves continue side by side up to the yield-point, when the large permanent set which then takes place completely upsets the former condition of the bar, as might have been expected. The temporary effect is roughly proportional to the elastic extension below the yield-point.

The conclusions to which I am drawn by these experiments are:—

(i.) Mechanical straining produces an "atomic disturbance" in a bar which increases regularly with the stress.

(ii.) For small stresses the disturbance is only partly permanent, but as the yield-point is neared it becomes wholly permanent.

(iii.) The magnetic properties of a loaded bar are in general different from those of the same bar unloaded, but there is a certain stress or range of stresses over which the bar has the same magnetic properties whether the load be on or off.

In Experiment I. the range of stress referred to in (iii.) is about 15 to 22 tons per square inch, the latter being the yield-point; and in Experiment III. it is about 10 to 15 tons per square inch, the latter being the yield-point. In Experiment II. the critical stress appears to coincide very nearly with the stress at the yield-point.

It is interesting to compare these results with those obtained by Joule. In his 'Scientific Papers,' pp. 253–256, Joule shows that an iron or steel bar elongates on being magnetized, but that if the bar is strained, the effect is reduced until, at a certain load, no effect is observed, and if the load be further

increased, magnetization produces a shortening of the bar. These experiments were made with soft iron and steel wires.

Joule's experiments show that magnetization produces a minute elongation of a bar, those quoted above show that mechanical stress increases the magnetization of a bar, *i. e.* mechanical stress produces a change similar to that produced by magnetization. It would seem, then, that Joule's critical point of no elongation (+ or −) must be reached when the molecular elongation produced by the mechanical stress is the same as that which would be produced independently by a certain given intensity of magnetization. For at that point, the molecular elongation having already been produced by mechanical stress, the effect of the given magnetization would be nil, *i. e.* there would be no further elongation (+ or −). Now, taking an intensity of magnetization, denoted by 5 in Joule's experiments, we see that this produces an elongation in a 12 inch length of soft iron wire (0·25 in. diam.) of $\frac{4}{150,960}$ in.; assuming Young's modulus for the iron at $13 \times 10^3$ tons per square inch, the mechanical stress required to produce this elongation would be about 0·03 ton per square inch.

According to Joule's experiments the critical stress is at about 6 tons per square inch, *i. e.* in order to produce this molecular elongation by mechanical means we require an elongation of the bar 200 times as great as that which accompanies the same effect produced by magnetization.

We are thus dealing with two distinct kinds of elongations—firstly, that produced by a relative motion of the molecules; and secondly, that produced by a straining of the molecules themselves.

It is clear that if the atomic displacement should be permanent, there would be a permanent change in the physical and chemical properties of the iron; and as there certainly is a change produced by permanent set, it is highly probable that we must look to such a straining of the molecule to account for it.

Thus, taken in conjunction with Osmond's experiments, those quoted above would seem to show that the increase in the value of the limit of elastic resistance with permanent strain is due to a permanent straining of the individual molecules.

## Experiment I.—Steel Bar.

| Load. | Micrometer. | Time in seconds of 20 vibrations. | $\frac{N^2-x^2}{10}$. | Load. | Micrometer. | Time in seconds of 20 vibrations. | $\frac{N^2-x^2}{10}$. |
|---|---|---|---|---|---|---|---|
| 0·0 | 1·417 | 24·9 | 218 | 0·0 | 1·418 | 18·9 | 389 |
| 0·1 | 1·417 | 24·85 | 219 | 5·4 | 1·457 | 18·7 | 398 |
| 0·2 | 1·417 | 25·0 | 217 | 0·0 | 1·418 | 18·7 | 398 |
| 0·4 | 1·418 | 24·8 | 221 | 0·0 | 1·418 | 18·65 | 400† |
| 0·0 | 1·417 | 24·85 | 219 | 5·6 | 1·458 | 18·65 | 400 |
| 0·6 | 1·420 | 24·75 | 221 | 0·0 | 1·418 | 18·6 | 403 |
| 0·8 | 1·420 | 24·6 | 224 | 5·8 | 1·463 | 18·7 | 398 |
| 1·0 | 1·422 | 24·55 | 225 | 0·0 | 1·420 | 18·5 | 407 |
| 0·0 | 1·417 | 24·9 | 219 | 6·0 | 1·465 | 18·3 | 416 |
| 1·2 | 1·424 | 24·1 | 234 | 0·0 | 1·420 | 18·5 | 407 |
| 1·4 | 1·425 | 23·7 | 243 | 6·2 | 1·465 | 18·35 | 414 |
| 1·6 | 1·426 | 23·35 | 250 | 0·0 | 1·420 | 18·4 | 412 |
| 1·8 | 1·427 | 22·4 | 273 | 6·4 | 1·467 | 18·2 | 421 |
| 2·0 | 1·428 | 21·8 | 289 | 0·0 | 1·421 | 18·55 | 405 |
| 0·0 | 1·417 | 22·6 | 268 | 6·6 | 1·469 | 18·3 | 416 |
| 0·0 | 1·417 | 22·5 | 271* | 0·0 | 1·421 | 18·3 | 416 |
| 2·2 | 1·430 | 20·9 | 316 | 6·8 | 1·470 | 18·0 | 431 |
| 2·4 | 1·431 | 20·55 | 327 | 0·0 | 1·421 | 18·6 | 403 |
| 2·6 | 1·433 | 20·4 | 332 | 7·0§ | | | |
| 2·8 | 1·434 | 20·3 | 336 | 0·0 | 1·455 | 18·8 | 394 |
| 3·0 | 1·436 | 19·85 | 352 | 7·0§ | | | |
| 0·0 | 1·417 | 20·7 | 322 | 0·0 | 1·507 | 19·2 | 377 |
| 0·0 | 1·417 | 20·75 | 321* | 7·0§ | | | |
| 3·2 | 1·437 | 19·6 | 361 | 0·0 | 1·538 | 19·4 | 369 |
| 3·4 | 1·438 | 19·5 | 365 | 0·0 | 1·538 | 19·5 | 365‡ |
| 3·6 | 1·439 | 19·65 | 359 | 7·7 | 2·095 | 17·95 | 433 |
| 3·8 | 1·440 | 19·6 | 361 | 0·0 | 2·036 | 25·35 | 210 |
| 4·0 | 1·442 | 19·45 | 367 | 8·0 | 2·178 | 16·5 | 515 |
| 0·0 | 1·417 | 20·05 | 344 | 0·0 | 2·112 | 25·05 | 216 |
| 0·0 | 1·417 | 19·9 | 350* | 8·3 | 2·323 | 16·8 | 497 |
| 4·2 | 1·444 | 19·1 | 381 | 0·0 | 2·248 | 25·45 | 209 |
| 0·0 | 1·417 | 19·75 | 355 | 8·6 | 2·455 | 16·65 | 506 |
| 4·4 | 1·446 | 19·15 | 379 | 0·0 | 2·374 | 25·7 | 204 |
| 0·0 | 1·417 | 19·45 | 367 | 9·0 | 2·692 | 17·05 | 482 |
| 4·6 | 1·451 | 19·1 | 381 | 0·0 | 2·616 | 26·4 | 193 |
| 0·0 | 1·418 | 19·5 | 365 | 9·3 | 2·981 | 16·8 | 497 |
| 4·8 | 1·452 | 18·8 | 394 | 0·0 | 2·893 | 26·35 | 194 |
| 0·0 | 1·418 | 18·9 | 389 | 10·0 | ..... | 17·4 | 462 |
| 0·0 | 1·418 | 18·9 | 389† | 0·0 | ..... | 27·5 | 177 |
| 5·0 | 1·453 | 18·85 | 391 | 10·5 | ..... | 17·35 | 465 |
| 0·0 | 1·418 | 19·05 | 383 | 0·0 | ..... | 28·0 | 170 |
| 5·2 | 1·455 | 18·65 | 400 | 10·87 | ..... | 18·1 | 426‖ |

* After 10″.
† After 5″.
‡ After 17 hours.
§ Load removed after small permanent set.
‖ After fracture.

## Experiment III.—Wrought-iron Bar.

| Load in tons. | $n$. Time in seconds of 20 vibrations. | $n^{-2} . 10^5$. | Load in tons. | $n$. Time in seconds of 20 vibrations. | $n^{-2} . 10^5$. |
|---|---|---|---|---|---|
| 0·0 | 17·25 | 336 | 0·0 | 13·2 | 574 |
| 0·5 | 16·8 | 354 | 2·7 | 13·25 | 570 |
| 0·0 | 17·1 | 342 | 0·0 | 12·85 | 606 |
| 0 0 | 16·9 | 350 * | 3·0 | 13·0 | 592 |
| 0·7 | 15·25 | 430 | 0·0 | 13·3 | 565 |
| 1·0 | 14·05 | 507 | 3·12 | 12·75 | 615† |
| 0 0 | 14·7 | 463 | 0·0 | 14·85 | 453 |
| 1·3 | 13·05 | 587 | 3·4 | 12·75 | 615 |
| 1·6 | 13·15 | 578 | 0·0 | 15·2 | 433 |
| 0·0 | 13·5 | 549 | 3·8 | 12·85 | 606 |
| 2·0 | 12·95 | 596 | 4·2 | 13·55 | 545 |
| 0·0 | 12·95 | 596 | 0·0 | 16·25 | 379 |
| 2·2 | 13·1 | 583 | 4·4 | 13·55 | 545 |
| 0·0 | 13·4 | 557 | 0·0 | 15·95 | 393 |
| 2·4 | 12·8 | 610 | | | |

* After one hour.

† After the permanent set.